DETERMINATION AND SPECIATION OF TELLURIUM IN ENVIRONMENTAL SAMPLES USING HYDRIDE GENERATION ATOMIC FLUORESCENCE SPECTROSCOPY (HG-AFS)

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Abstract

This thesis focuses on developing a new method to measure trace tellurium (Te) in different environmental samples such as lake waters, mine tailings and sediments. The developed technique is based on Hydride Generation Atomic Fluorescence Spectroscopy (HG-AFS), a technique that can measure low concentration of Te and also allows for Te speciation at low cost and high efficiency in various environmental samples.

To validate the method that could be used to determine Te speciation in various types of environmental samples, a series of tests has been designed for finding the best conditions to measure Te(IV) using HG-AFS and obtain accurate and reliable results. Those tests include the stability of the signal, the acidity of the solution, the volatility of Te after digestion of solids, the reduction from Te(VI) to Te(IV), the detection limit of the technique, and the validity of two digestion methods under the optimum (HG-AFS) instrumental settings.

An interference study including the most common elements in the Earth's crust such as (Ni, Fe, Pb, Cr, Cu, Co, Zn, Mn and Mo) was also performed. The results of this study showed that Cu(II) can severely interfere with Te quantification decreasing the Te signal to almost zero. Therefore, different masking agents such as 8-hydroxyquinoline, 1,10-phenanthroline, urea and thiourea were tested to reduce and eliminate this interference.

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Chapter 1

1. Introduction

The detection and measurement of elements in environmental and biological samples is very important to reveal the roles of these elements in nature. This becomes especially pertinent to elements that are present in trace amounts in the environment, but nonetheless have several applications or potential toxicities. Tellurium (Te) is one such element which has been found to have known applications in metallurgy, semiconductor technology, anticancer biology and drug development (Cunha et al., 2009). Tellurium can be found in soil, water and gaseous emissions and is part of the sludge that is generated from copper and gold ores following elemental extraction. Tellurium exists in several oxidation states and this property is responsible for many of its known functions/applications. Several methods have been successfully used for the determination and detection of Te from its natural sources. Some of these include atomic absorption spectrometry, inductively-coupled plasma - mass spectrometry (ICP-MS) and hydride generation coupled to atomic fluorescence spectroscopy (HG-AFS). Each of these techniques has certain advantages and disadvantages over the others and over time, several methods for sample pre-concentration, atomization and detection have been developed to neutralize some of the interference effects and limitations caused by the various techniques. The use of hydride generation as a method of derivatization of the analyte into a volatile hydride before detection has proven to be especially useful for the determination of trace elements that can form hydrides. The combination of hydride generation with atomic fluorescence spectroscopy has been shown valid and efficient for the detection of Te in the microgram per litre (ppb) range (Feng & Fu, 1998). Further understanding of the properties of this element and the existing detection methods will aid in the development of technological innovations that yield improved sensitivity.

1.1. Tellurium – an element with great potential but little renown

1.1.1. Discovery and geochemistry

Tellurium is a semi-metallic substance and it forms part of the group of chalcogens which include sulfur and selenium. The term 'tellurium' is derived from the latin term, 'tellus' which means earth. Te was discovered in 1782 by a chemist and mine inspector, Franz-Joseph Mueller von Reichenstein, in Transylvania. Reichenstein thought that the substance he had isolated from an ore of gold was antimony. But when he saw that this element did not resemble antimony in any of its properties, he named it *metallum problematicum* or *aurum paradoxicum.* Later, a German chemist, M. H. Kalproth mentioned this element in a publication and called it tellurium. (Cunha et al., 2009)

There is still a lot to be discovered about the geochemistry of Te. In the Earth's crust, Te is as abundant as metals like silver and gold and is present at a concentration around 27 μg/kg (ppb) (Ba et al., 2010). Tellurium is isolated from the sludge that is produced after copper extraction from ores. The alkaline extraction is complex since the method employed will depend upon what other compounds or elements are present. It is also present as an impurity in gold and silver ores. There seems to be an uneven distribution of Te on the earth. For instance, although the overall abundance is thought to be 27 μg/kg, in some areas like the Dongping village in North China, the amount of Te found in the gold deposits reaches an average of 671 μg/kg (Hua, 2000). The concentration of Te in natural water sources is below the μM range (Pedro et al., 2006). Plants have also been shown to accumulate Te to the mg/kg range. The amount of Te found in the world differs from one region to another and between land, water and air sources. (Table 1-1.)

1.1.2. Basic chemistry and properties

Tellurium belongs to the 5^{th} period and group 16 of the periodic table and has oxygen, sulfur and selenium belonging to the same group. It has an atomic number of 52 and the electronic configuration [Kr] $4d^{10}5s^{2}5p^{4}$ (Ba et al., 2010). Being so low in the group, it exhibits a combination of metallic and non-metallic qualities and is hence called a metalloid or a semi-metallic element. The elemental form of Te can be either brownish-black or metallic silver and both allotropes occur in nature (Ba et al., 2010). Naturally occurring Te is a combination of 8

isotopic forms with rounded atomic masses of 120, 122, 123, 124, 125, 126, 128 and 130 a.m.u., respectively. Mass spectrometry analysis has shown that the most abundant form of Te is ^{130}Te at 34.1% and the least abundant is ^{120}Te at 0.1% (Ba et al., 2010).

Table 1-1. Concentration of Te from selected soil, water and air emissions (modified from Ba et al., 2010).

Soil sources	µg/kg
San Joaquin soil (California, USA)	90
Guangxi area (China)	70
Atmospheric deposition (Norway)	5.2
Water sources	µg/kg or µg/L
River and harbor sediments	<0.001
Geothermal waters (New Zealand)	<0.001
Air sources	µg/kg
Soil gases near ore deposits (Germany)	0.000003
Emissions near waste treatment facilities	0.0001
Emissions from industrial sludge fermenters	0.1
Sewage gas (Germany)	0.001

Tellurium shows many similarities with the other chalcogens such as As S and Se; Te exists in a number of different oxidation states. In the most reduced state it is seen as hydrogen telluride (H_2Te), with an oxidation state of -2. In Na_2Te_2, the ditelluride anion Te has a -1 oxidation state. Higher oxidation states and the cationic nature of Te are seen in its oxides, for example, Te has a +4 oxidation state in TeO_2 and is +6 in TeO_3. Further oxidation of Te from these states leads to the formation of tellurous (H_2TeO_3) and telluric acids ($Te(OH)_6$) and the salts tellurites and tellurates respectively. However, unlike sulfur, the oxidation states +4 and +6 of Te have comparable stabilities and this redox behavior becomes vital for some of its

biological activities. (Ba et al., 2010). Tellurium can also form numerous inorganic and organic complexes.

1.1.3 Tellurium in biology

Since the 1920s, published literature suggests the use of Te as a therapeutic agent for diseases like syphilis and leprosy. Tellurium has also been shown to have antimicrobial properties and to reverse the sickling of red blood cells in sickle cell anemia patients. In the late 1980s, an AIDS cocktail containing Te compounds was made. This drug, called AS-101, has been shown to modulate the expression of interleukins like IL-2, -5 and -10 and gamma interferon. More recently, Te related therapeutic effects include hair growth, protection from apoptosis, and promotion of neuronal cell survival after ischemia and protection of dopaminergic neurons in Parkinson's disease (Cunha et al., 2009).

Much of the exposure to Te compounds is occupational and via inhalation, for example, among metal foundry workers. Accidental ingestion of Te compounds has also been documented in a few cases (Hazardous Substance Data Bank, HSDB). The organs that show Te accumulation after exposure include the liver, spleen and kidneys. Tellurium(IV) has a physiological half-life of two months and exposed individuals may also show significant amounts of Te in their soft tissue, skin and body fluids, from where Te is transformed and eliminated in its dimethylated form. (MAK Value Documentation, 2006).

Toxicity studies for Te have been conducted by several authors and it has been shown that low concentrations of Te, either inhaled or ingested, can cause acute or chronic toxicity depending on the duration of exposure. Compared to selenium, Te is less soluble and in its reduced form, it is easily degraded by exposure to light or air. This has been suggested as reasons for the apparent lower toxicity of Te compared to selenium (Cunha et al., 2009). The common signs and symptoms of chronic Te toxicity include a sour garlicky odor to the breath and feces, dry and metallic taste in the mouth, tiredness, sleeplessness and nausea. Acute exposure can also cause these symptoms, in addition to respiratory distress and edema, retinal changes and in rare cases, death. (HSDB, 1971)

Several mechanisms have been reviewed for the toxicity of Te in the body. One of the ways by which Te acts in the body is by inhibiting cholesterol synthesis. Tellurium and its oxyanionic forms interact with the enzyme squalene monoxygenase, which is the rate-limiting enzyme in the cholesterol biosynthetic pathway. This enzyme catalyzes the oxidation of squalene to squalene-2,3-oxide. By blocking this enzyme, cholesterol is not synthesized. Cholesterol is needed for the generation of cell membranes and in neurons, it is the chief constituent of the myelin sheath that provides insulation and allows for rapid nerve impulse conduction. Lack of cholesterol leads to demyelination and can cause neuropathy like symptoms. At the molecular level, Te, both as itself and in a methylated form, binds to active site cysteine residues at positions 490 and 557 in squalene monoxygenase causing inhibition of the enzyme (Cunha et al., 2009; Ba et al., 2010). In a similar manner, methyl tellurium compounds also inhibit the enzyme squalene epoxidase in Schwann cells that surround axons of nerve fibers. (Ba et al., 2010). Organotellurium compounds like diphenyl ditelluride exert their neurotoxic and teratogenic effects in rats by interacting with –SH groups present in enzymes like Na^+- and K^+- ATPase (Ba et al., 2010).

Apart from their toxic effects, Te compounds have been shown to have antioxidant effects as well. This has been observed in the case of organic Te compounds and their interaction with the glutathione peroxidase system. Glutathione is a natural reducing agent present in cells that helps to scavenge free radicals produced as a result of normal metabolic activities. The conversion of glutathione from its reduced to oxidized form is catalyzed by the glutathione peroxidase enzyme. The active site of this enzyme has a selenium atom. It has been found that organic Te compounds can act as a selenium mimic and take its place in the enzyme. In fact, it has been shown that aryl derivatives of Te can augment the antioxidant capabilities of the enzyme. (Cunha et al., 2009). Other antioxidant systems that are improved by Te compounds include the thioredoxin / thioredoxin reductase system. This is particularly interesting as this system is a well-known target of many chemotherapy drugs. (Cunha et al., 2009).

Furthermore, exposure to Te compounds does not affect fertility in rats, although fetal hydrocephalus was observed when elemental Te was given at a dose between 165 and 220 mg/kg body weight during gestation. Tellurium dioxide also adversely affected neonatal development

while potassium tellurate and cadmium telluride did not have any effect. (MAK Value Documentation, 2006).

1.1.4 Detection of tellurium – Techniques

Given its low terrestrial abundance and its toxicity in mammalian systems, the accurate and precise determination of Te is extremely important. Several techniques have been developed for this purpose and differ in the type and amount of raw material needed, sensitivity and time taken for detection. The first step for the detection is generally pre-concentration of the ore/raw material so that trace amounts of Te can be accurately detected and eluted. Several methods have been proposed over the years. It has been proposed that trace concentrations of inorganic Te in the air can be detected by first adsorbing the element onto gold beads and using cationic and anionic resins to separate it. Once separated on these resins, Te can be eluted by changing the pH of the reaction mix. Then the element can be detected by graphite furnace atomic absorption spectrometry (GFAAS).

Another method of pre-concentration is by co-precipitating Te with metal oxides like those of lanthanum and iron. Pedro et al., (2006) used $La(OH)_3$ to co-precipitate Te from air samples followed by its adsorption onto XAD resins. The authors found that the XAD resin showed 72% efficiency in adsorbing Te and had an upper limit of detection of 66 ng/L (Pedro et al., 2006). Using a similar principle, (Donaldson and Leaver 1990) utilized hydrous ferric oxide to co-precipitate Te present in copper ores. The method involved dissolving the ore in an ammoniacal medium, co-precipitating Te with ferric oxide, dissolving the precipitate in hydrochloric acid and using GFAAS to detect Te. This method was considered advantageous as it could be directly applied to any terrestrial samples suspected of containing as low as 10 pg of Te for each gram of the sample. Other metal oxides and salts used for co-precipitating trace elements such as Te include mercury, tin, magnesium (Yildirim et al., 2012) and aluminum (Duan et al., 2003). Iron and aluminum oxides are favored over other metal oxides because of their ability to co-precipitate a large number of trace elements and $Fe(OH)_3$ shows a superior separation efficiency (Duan et al., 2003).

Yet another way by which pre-concentration is done is by online *in situ* trapping of gaseous H_2Te onto graphite tubes. In this process, the analyte is atomized in the presence of a strong reducing agent, preferably sodium borohydride ($NaBH_4$) and the H_2Te that is generated is trapped on graphite tubes (Yildirim et al., 2012). This method has the advantages of high sensitivity, reproducibility, low atomization interferences and easy operation (Yildirim et al., 2012). Further, the technique can be modified by using graphite tubes pretreated with elements like iridium (Ir), magnesium (Mg), zirconium (Zr), niobium (Nb) and palladium (Pd) either singly or in combination. This increases sensitivity and allows detection as a level as low as 0.007 ng of Te (Yildirim et al., 2012). Xi et al. (2010) used this principle to trap Te onto quartz tubes that were incorporated with a tungsten (W) coil. The use of the tungsten coil for hydride trapping has been considered more advantageous than the use of graphite furnace because W has an easier availability and a better resilience. Also, it helps to safe energy and power as it heats up faster than graphite. This technique of hydride trapping with tungsten was developed independently by de Souza et al. (2007) and Ataman (2008) as cited in Xi et al. (2010). A similar principle was used by Matusiewicz and Krawcyzk (2007) for the determination of Te in sediment samples, coal fly ash and garlic. They used the air-acetylene flame to atomize the analyte and used *in situ* hydride trapping in a customized PVC/PTFE tube and then used atomic absorption spectrometry to detect the levels of Te. They found that the use of this technique allowed for the detection of Te in fly ash and garlic to the precision levels of 1.863 ± 0.112 mg/kg and 0.058 ± 0.005 mg/kg, respectively. The authors also detected no interference due to matrix effects or technical errors (Matusiewicz & Krawcyzk, 2007).

As Te exists in various oxidation states and these differ from each other in their properties, it is also important to have techniques that not only detect total Te levels in the analyte, but also provide information regarding speciation. For example, the bioavailability and toxicology profile of Te(IV) is different from that of Te(VI) (Kuo & Jiang, 2008). For this purpose, Kuo and Jiang (2008) used a combination of ion exchange chromatography to separate the different oxidation states of Te and then used inductively coupled plasma mass spectrometry (ICP-MS) to detect the different species in samples of milk, rice flour and urine. In their analysis, they used a pneumatic nebulizer to vaporize the analyte sample and ammonium citrate was used as the mobile phase in chromatography. By standardizing the concentration and the pH of the

mobile phase, they were able to retain the Te(IV) species onto the matrix and separate these from the others. A similar principle was also used by Yu et al. (2003) whereby the analyte was allowed to interact with ammonium pyrrolidine dithiocarbamate (APDC) under low pH conditions. This caused Te(IV) species to be retained on the solid phase extraction cartridge and allowed Te(VI) to flow through. Detection was again performed by ICP-MS (Yu et al., 2003).

Tellurium determination by hydride generation atomic absorption spectroscopy in nickel and copper alloys has been done by Liu et al. (2002). The authors used a 5% (w/v) solution of ascorbic acid as a reducing agent to generate tellurium hydride and then extracted Te from the copper alloys using the chelating agent, N-nitroso-N-phenylhydroxylamine (cupferron). They then used atomic absorption spectrometry to detect Te. One of the limitations with cupferron dependent extraction for Te is that it is also pH dependent with the best extraction occurring at around pH 7. Also, this is a novel technique and therefore requires much optimization before it can be used routinely (Liu et al., 2002).

1.2 Atomic Fluorescence Spectroscopy (AFS)

Atomic Fluorescence Spectroscopy is an analytical technique that is very sensitive for the detection of trace amounts of elements in different environmental samples. This technique exploits the idea that when the sample is exposed to electromagnetic radiation, the atoms go from the ground energy state to an excited state. When these come back to the ground state, they emit fluorescence. The energy diagram is provided in figure 2. The emission is unique to each element and can thus be used to detect it. The main advantage of this technique over atomic absorption or ICP-MS is that there is no background signal produced, the instrumentation is relatively inexpensive and multi-elemental analysis can be done. Additionally, as the fluorescence intensity is proportional to the concentration of the element, this method can be used for the quantitative analysis of elements.

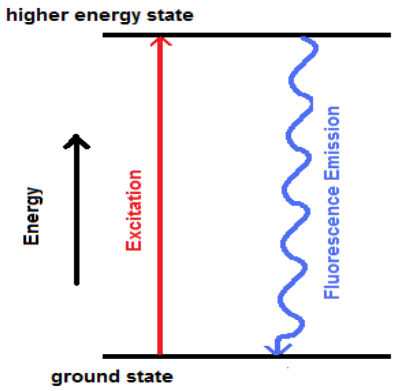

Figure 1-1. Basic energy diagram representing the principle of AFS (redrawn from IGNOU)

1.2.1. Discovery of AFS and types of fluorescence energy transitions

The potential of AFS was initially suggested by Alkemade in 1962 and in a few years, the technique was practically demonstrated by Winefordner and West in 1964 (Ebdon et al., 1998). While the overall energy diagram can be approximately represented as in Figure 1-1, it has been determined that the fluorescence spectra of different elements are different. The different fluorescence energy transitions include resonance fluorescence, Stokes direct line fluorescence, stepwise line fluorescence, two step excitation or double fluorescence, thermal fluorescence and sensitized fluorescence (IGNOU). The energy transfer diagrams of the different transition types are summarized in Figure 1-2. In resonance fluorescence, the wavelengths for excitation and emission remain the same. This is seen in the magnesium atom. Radiation scattering and the associated false high detections are the limitations of this type of energy transition. In Stokes direct line fluorescence, the emission wavelength is less than that of excitation and after emitting direct line fluorescence to an intermediate energy level, the remaining energy is dissipated from the excited atoms through a radiation-less transfer. Thallium emits its fluorescence energy in this manner (IGNOU). The opposite effect is seen in stepwise line fluorescence transfer. Here, after excitation, the atom returns to an intermediate energy state through radiation-less means and then gives out fluorescence when it returns from this mid-level to the ground state. An example for this type of energy transition is seen in sodium (IGNOU).

In double fluorescence, the excitation is a two step process, done by lasers. The first laser excites the atom from the ground to excited state 1. The second laser increases the energy of the atom so that it goes up from excited state 1 to 2. When the atom comes back to the ground state, it emits fluorescence. Thermal or anti-Stokes fluorescence is similar to double fluorescence in that, the atom is excited twice, initially by radiation and finally by heat in a radiation-less manner. This transfer is different from double fluorescence however because fluorescence can occur when the atom loses energy from either or both of the excited states (IGNOU).

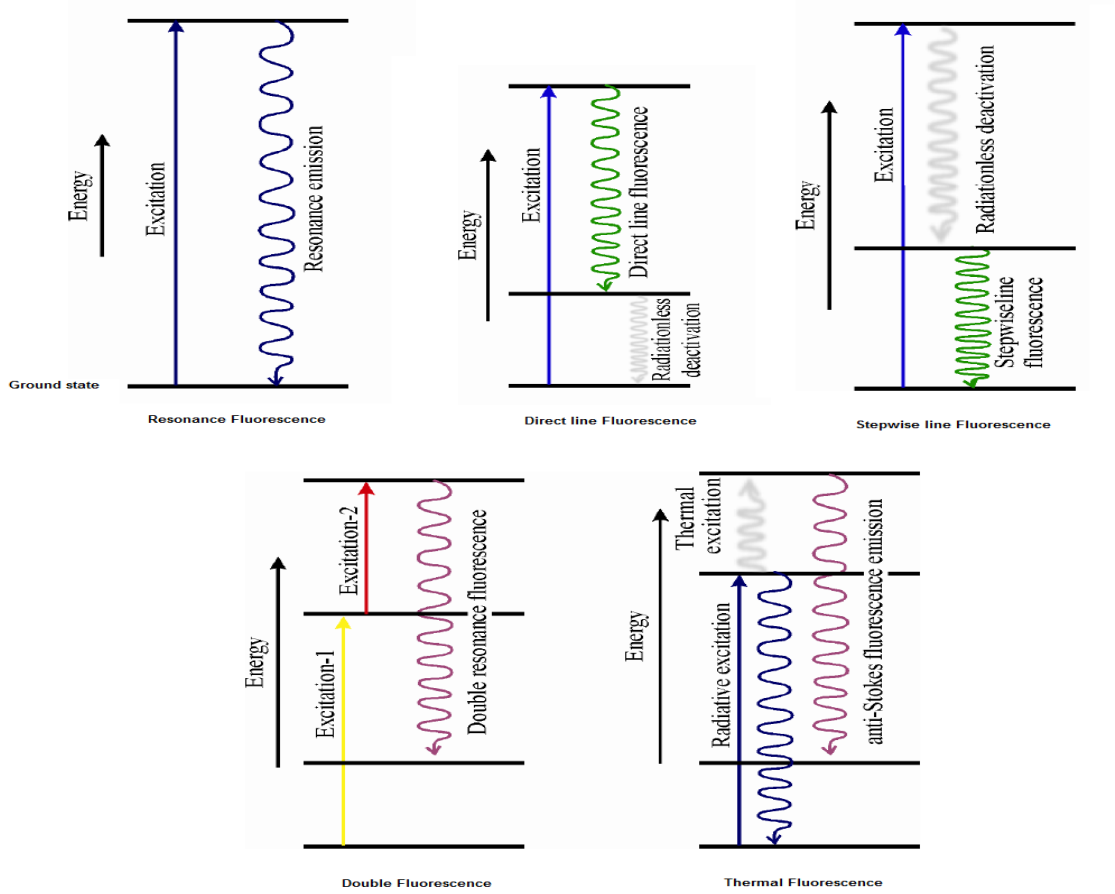

Figure 1-2. The different fluorescent energy transitions (Ebdon et al., 1998)

1.2.2. Principle of AFS

The overall rationale behind AFS is as follows. The sample to be analyzed, also called the analyte is atomized with the help of a flame or furnace. These atoms are in the ground state and are excited by using either a continuous or a monochromatic wavelength source. The atomic fluorescence is then measured using a relevant detection and quantification device. The fluorescence intensity is proportional to the amount of the element of interest in the analyte, at low concentrations. This is summarized by the following equation (Ebdon et al., 1998):

$$I_f = k\varepsilon I_0 C$$

Where

I_f = fluorescence intensity

k = constant

ε = quantum efficiency

I_0 = radiation source intensity at the wavelength for absorption

C = concentration of the atoms

However, beyond a threshold concentration, problems of self absorption and quenching effects occur and that may affect the efficiency of this procedure, although AFS can be modified to reduce these effects (IGNOU).

1.2.3. Instrumentation

The components of an AFS setup are a source of radiation, an atomic reservoir where analytes are atomized, a monochromator to select the appropriate wavelength, a detector and a readout system (Figure 1-3).

The radiation source can be continuous like a tungsten halide lamp, which has the benefit of allowing for multi-element analysis but lacks high radiant density for sensitive detection. The use of hollow cathode lamps provides single line radiation and hence overcome the sensitivity

limitation of the continuous radiation sources, but cannot be used for multiple element analysis (IGNOU).

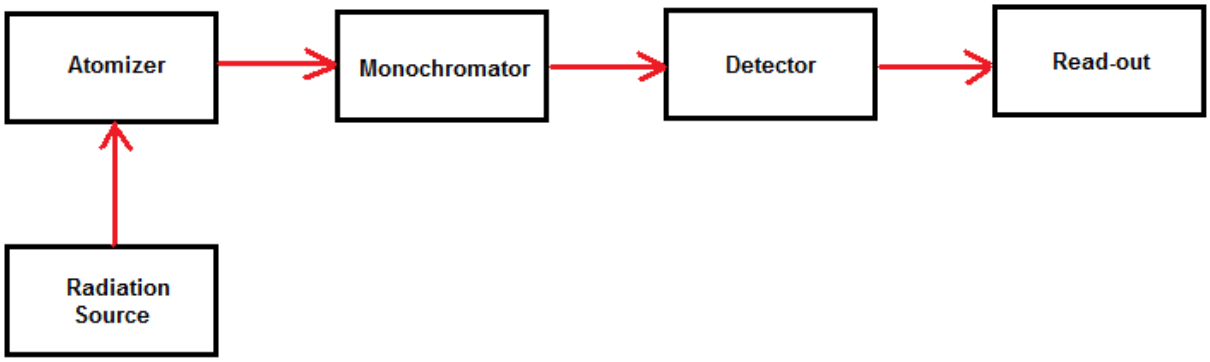

Figure 1-3. Schematic representation of an AFS setup (modified and redrawn from IGNOU).

The atomization of the analyte is one of the most important steps in AFS and this is done in an atom cell or reservoir. The most commonly used atomizer is the hydrogen diffusion flame as this provides very low background noise. Also, the stable temperature that is held by this flame (350 - 400°C) allows for good detection. Other ways by which atomization of the analyte is done include the use of a combination of acetylene and nitrous oxide or hydrogen, oxygen and argon in atomic absorption spectrometry. These combinations are used as higher temperatures are achieved, although there is a greater chance of getting higher background noise as well. The graphite furnace, if used for generating atoms, provides a greater sensitivity than flame atomizers and requires smaller amounts of analyte. This advantage is also seen with cold vapor cells where the analyte is reacted with $SnCl_2$. Finally, hydride generation (explained in more detail in the following section) is used for those elements such as As, Se, Sb and Te that can form hydrides when reacted with $NaBH_4$.

Once atomized, the sample is excited using pre-calculated and optimized wavelengths of light, which lie between the UV and visible range in the electromagnetic spectrum for AFS. Diffraction gratings are primarily used for this purpose. Finally, the fluorescent emissions are detected by the use of photomultiplier tubes and displayed digitally.

There are merits and demerits to the use of AFS. The main advantage is that this technique offers minimum background effects, very good sensitivities for the detection of metalloids and can be used with solid, liquid and gaseous analytes. But, sample preparation is often time consuming and techniques like chromatography need to be used in combination with AFS to perform speciation analysis for elements like Te. Also, matrix effects and chemical interference can occur that can cause limitations to the sensitivity of the protocol (IGNOU).

1.2.4. Hydride Generation

Hydride generation is one of the routinely used techniques for the derivatization of analytes before subjecting them to atomic or fluorescence spectroscopy. In a simplified reaction for Te(IV), the oxidation state needed to form the hydride:

$$4\ H_2TeO_3 + 3\ BH_4^- + 3\ H^+ \rightarrow 4\ H_2Te + 3\ H_3BO_3 + 4\ H_2O$$

It can be used for elements such as arsenic, antimony, selenium, tellurium and others that are capable of forming hydrides. These hydrides are generated by exposing the analyte to a strong reducing agent. Zinc/hydrochloric acid mediated reduction, though initially used, is not preferred because this process needs an extra collection reservoir as part of the spectroscopic setup and is time-consuming. A more powerful reducing agent, sodium borohydrate is now commonly used as it eliminates all the above limitations. This reagent can be used to generate the hydrides of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin (Ebdon et al., 1998; D'Ulivo et al., 2011).

Hydride generation is a sensitive method of atomization, although it has several limitations. The first is called liquid phase interference. This happens when other elements such as copper, gold, nickel and cobalt present in the acid leachate liquid analyte also get reduced in the presence of $NaBH_4$ (Hall et al.,1997). This is a real concern, especially since it is known that copper and gold ores are good sources of Te. There are two methods by which this limitation can be reduced. The first involves complexing these elements with substances such as EDTA, tartarate and citrate, which is extremely time consuming and impractical. The second method to

reduce liquid phase interference is much simpler and requires the co-precipitation of the analyte with metal oxides like $La(OH)_3$ (Hall et al., 1997; Pedro et al., 2008; D'Ulivo et al., 2000)

Another limitation to the process of hydride generation is the gas phase interference that can occur when diatomic species are formed from two different elements in the analyte. This interference can either reduce the number of free atoms of the element of interest available for detection or can make them decay or degrade. Either way, this interference can lead to false negative values during detection. This limitation can be removed by increasing the temperature used for the atomization process (Hall et al., 1998).

1.3 Objectives of the research

The main objective of this thesis was to develop analytical protocols based on the technique of Hydride Generation coupled to Atomic Fluorescence Spectroscopy to measure with accuracy and precision the concentration of tellurium in various types of environmental samples. Solids such as lake sediments and mine tailings will be digested and measured and lakewater samples will be analyzed to measure the concentration of Te(IV) and Te(VI) or spiked with those two chemical species to determine the feasibility of the HG-AFS technique to measure both in natural waters.

Chapter 2

2. Methodology

In this chapter, all aspects related to experimental processes are described.

2.1. Reagents and preparation of solution

Chemical reagents used in this study are listed below and different solutions were prepared according to the following instructions.

2.1.1. Chemical reagents

(1) Standard of Te (IV) was prepared with Tellurium dioxide (TeO_2, Aldrich 99+%) and that of Te(VI) was prepared with telluric acid (H_6TeO_6, Aldrich, 97.5 – 102.5%)

(2) Sodium tetrahydroborate, ($NaBH_4$) 98%, Aldrich.

(3) Sodium Hydroxide (NaOH), A.R. Aldrich.

(4) Potassium Bromide (KBr), A.C.S, Assay min 99.0%, EM SCIENCE.

(9) Hydroxylamine hydrochloride ($NH_2OH.HCl$) 99% Aldrich.

(10) Hydrochloric acid (HCl), A.C.S, Assay 36.5-38.0%, Fisher Scientific.

(11) 8-hydroxyquinoline (C_9H_6NOH), assay not less than 99.5%, The British Drug Houses LTD.

(12) 1,10-phenanthroline hydrate ($C_{12}H_5N_2H_2O$), A.R., The British Drug Houses LTD

(13) Thiourea, $CS(NH_2)_2$, The British Drug Houses LTD.

2.1.2. Preparation of solutions

(1) Standard Te(IV) stock solution at 1000 mg/L: 0.06254 g of TeO_2 was dissolved in an HCl solution, fixed to 50.00 mL to obtain a final HCl 3.0M solution and stored in a HDPE bottle and kept in the refrigerator.

(2) Standard Te(VI) stock solution at 1000 mg/L: 0.0900 g of H_6TeO_6 in an HCl solution, fixed to 50.00mLto obtain a final HCl 3.0M solution and stored in a HDPE bottle and kept in the refrigerator.

(2) 0.7% (w/v) sodium tetrahydroborate solution in 0.1M NaOH: 7.0 g of $NaBH_4$ powder and 4.0 g of NaOH were dissolved in 1000 mL of distilled water. The solution was stable for at least 1 week at 4 ^{o}C.

(3) Concentrated hydrochloric acid was used to prepare a 3.0M HCl solution. Concentrated nitric acid and hydrofluoric acid were also used in this study to digest solid samples.

(4) For the interference study, all standard solutions (Ni, Cu, Mo, Mn, Cr(VI), Cr(III), Zn, Pb, and Fe) were prepared from their corresponding 10000 mg/L standards in 5% (v/v) HCl solutions.

2.2 Apparatus

2.2.1 Microwave digestion system

A Milestone Ethos 1600 URM, HPR 1000/10 (Bergamo, Italy) microwave digestion system was used for digestion and pre-reduction tests on Te(VI)

2.2.2. Hydride Generation - Atomic Fluorescence Spectrometer (HG-AFS)

A PSA 10.055 Millennium Excalibur equipped with a continuous flow hydride generation system and a boosted discharge hollow cathode lamp as the radiation source of atomic fluorescence detector was used to determine the concentration of Te(IV) in sample solution. Instrumental working conditions are given in Table 2-1.

The simplified work principle of this instrument can be presented as follows:

$$NaBH_4 + 3\ H_2O + HCl \longrightarrow H_3BO_3 + NaCl + 8\ H^* \xrightarrow{Te(IV)} H_2Te + H_2\ (excess)$$

where E is the analyte with oxidation state m, which may or may not be equal to n.

The hydride and excess hydrogen are swept out of the generation vessel using a stream of argon into a chemically-generated hydrogen diffusion flame. The hydrides are atomized and the resulting atoms are detected by atomic fluorescence spectroscopy. The concept of nascent hydrogen gas is not accepted by all researchers and it has been suggested the transfer of hydrogen from the borohydride to the analyte is a concerted step-by-step reaction (D'Ulivo et al. 2011).

Table 2-1 Instrument working conditions for HG-AFS.

Sample flow rate (mL/min)	7.5
$NaBH_4$ flow rate (mL/min)	4.5
Carrier solution (mol/L HCl)	3.0
Argon inner pressure (psi)	30
Argon flow rate (mL/min)	250
Carrier gas (Ar) (mL/min)	300
Dryer gas (Ar) (mL/min)	2.5
Hydrogen flow rate (mL/min)	120
Lamp current (mA)	15
Delay time (s)	13
Analysis time (s)	20
Memory time (s)	28
Signal type	Peak height

2.3. Optimal instrumental conditions

The best signal that can be obtained using a hallow cathode lamp to measure Te(IV) was tested by changing the primary and boost power of the lamp. The Te(IV) stock solution concentration was 1000 mg/L in 5% (v/v) HCl. From the 1000 mg/L Te(IV) solution, a 60 µg/L working solution was prepared in 3.0M HCl through successive dilutions.

2.3.1 Effect of hydrochloric acid concentration (HCl) on Te(IV) signal

Tellurium was analyzed under different concentration of HCl to determine the acidity that can provide the best signal using HG-AFS. Three different concentrations of Te of 20, 40 and 60 µg/L were tested in 2.0, 2.5, 3.0, 3.5 and 4.0M HCl, respectively.

2.3.2 Detection limit

To determine the detection limit for Te(IV) using HG-AFS it is very important to avoid excessive dilution in future experiments. Therefore, aliquots of 25.00 mL of different concentrations of Te(IV) from 50 to 200 ng/L were prepared in 3.0M HCl solution and analyzed using HG-AFS.

2.3.3 Tellurium linearity range

Aliquots of 25.00 mL of different concentrations of Te(IV) were prepared in 3.0M HCl solution and analyzed using HG-AFS to test the linearity of the technique.

2.4. Pre-reduction of Te(VI) to Te(IV)

Some commonly used reducing reagents were tested at room temperature with a maximum concentration of 0.602M for KI, 0.420M for KBr, 0.284M for ascorbic acid, 0.555M for oxalic acid in a solution that contained 60 µg/L of Te(VI) in 3.0M HCl. These solutions were set on the counter at room temperature (25 °C) for 24 hours before the Te concentration could be determined.

2.4.1. Volatility of tellurium in HCl matrix subjected to a microwave pre-reduction

The test on the possible losses of Te during digestion in HCl was conducted as below.

An aliquot of 25.00 mL of 10 µg/L Te(IV) in 3.0M HCl was transferred into a Teflon digestion vial and subjected to microwave treatment (20 – 110 ^{o}C in 10 min, kept at 110 ^{o}C for 10 min, vented for 20 min to reduce the pressure before being removed from the microwave oven).

Two groups of tests were designed and each group included 5 samples. For Group One, the sample solution in the digestion vial was transferred in time sequence into a pre-cleaned 50.0 mL polypropylene centrifuge tube without previous cooling. For Group Two, the sample assembly together with the vials and the rotor segments were completely cooled down in an icy water bath before the digestion vials were opened. The thoroughly cold solutions were transferred into 50.0 mL polypropylene tubes. The Te(IV) in the sample solutions of the two groups were determined by HG-AFS.

2.4.2 Pre-reduction using 3.0M HCl

Attempts to reduce Te(VI) to Te(IV) were performed. Two groups of tests were designed. For group one, different concentrations of Te(IV) were prepared in 3.0M HCl in a final volume of 25.00 mL. For group two, it was the same as for group one but with Te(VI) and the samples were subjected to a microwave treatment.

The tests using the microwave digestion system included: from room temperature to 110 $^{\circ}$C in 10 minutes; kept at 110 $^{\circ}$C for 15 minutes and cooling for 20 min before placing the samples in an ice bath for one hour.

2.4.3 KBr as reducing agent at 100 ^{o}C under microwave conditions

In this study, KBr was used to reduce Te(VI) to Te(IV). One series was prepared using 0.17M KBr in 3.0M HCl with different concentrations of Te(VI) added into each sample; the final volume was 25.00 mL. The sample was treated in the microwave digestion system from room temperature to 100 °C in 10 min, kept at 100 °C for 15 min and allowed to cool for 20 min before being put in an ice bath for one hour before the digests were transferred. The Te(IV) signals were measured by HG-AFS and compared with a standard calibration curve produced by Te(IV).

2.4.4 Pre-reduction under different concentrations of HCl and higher temperatures.

Another approach was taken to pre-reduce Te(VI) to Te(IV). This new method was based on trying different molarities of HCl under higher temperatures using the microwave treatment. The Tellurium(VI) concentration in this experiment was constant at 10.0 µg/L and concentrations of HCl of 2.0, 2.5, 3.0, 3.5 and 4.0M were prepared from concentrated HCl; the microwave program was from room temperature to 110 °C for 10 min, kept at 110 °C for 15 min and allowed the digest to cool down under vent condition for 20 min. The digest assembly was cooled down in an ice bath before the solution was transferred. Signals were recorded and recoveries calculated.

2.5 Interference of metal ions on Te(IV) determination and masking agent selection

The Tellurium (IV) interference study was done with some common elements encountered in the earth crust, namely Cr (VI), Cu(II), Fe(II), Mn(II), Ni(II), Pb(II), Zn(II) and Mo(VI) at different concentrations but using a constant 10.0 µg/L solution of Te (IV) in 3.0M HCl. A blank solution of mixed metal ions in 3.0M HCl was always carried as a control. The prepared solutions were measured using HG-AFS. All the elements were prepared from 10 000 mg/L stock solutions and then diluted to the desired concentration levels.

2.5.1 Selection of a masking agent

Several masking agents were tested and series of experiments were performed. In all experiments, the concentration of Te(IV) kept constant at 10 µg/L. A larger volume of solution containing the given concentration of masking agent was prepared in 3.0M HCl. An aliquot of 6.25mL of such a solution was transferred into a 25.00 mL volumetric flask, then small quantities of the Te(IV) standard solution and interfering metal solution were spiked in the solution and fixed with the solution to 25.00 mL with the masking agent solution. The concentration of Te(IV) used in the text was constantly kept at 10 µg/L.

2.6 Determination of total Te in Sudbury lake waters

Two water samples of 2.5 L were collected in May 2013 from Kelly Lake and Ramsey Lake in Sudbury. Samples were filtered through a 0.45 µM Millipore membrane. For direct

measurement, 6.25 mL of 12M HCl was added into a 25.00 mL volumetric flask and the rest of the volume was the filtered lake water sample. The matrix of the sample was then 3.0M HCl and the dilution factor of the sample was 1.33. In another series, an aliquot of 6.25 mL HCl (12M) was added into a 25.00 mL volumetric flask, known amounts of Te(IV) or Te(VI) were spiked and the volume was fixed to 25.00 mL with the filtered lake water. The sample matrix was 3.0M HCl and dilution factor was 1.33. To determine the possible concentration of Te(VI), the samples were pre-reduced in the microwave oven.

2.7 Digestion method for mine tailings, lake sediments and certified reference materials

2.7.1. Comparison of two methods for total Te measurement in tailings and sediments

To determine the concentration of total Te in solid samples, different digestion methods were tested on tailings, lake sediments and certified reference materials. Tailing samples were collected from the Vale tailing site in 2011. They were dried slowly at room temperature and ground with a ring pulverizer to pass through a 20-mesh (0.84 mm) sieve. Sediments included freeze-dried compound samples from two Sudbury area lakes, McFarlane and Clearwater and 5 other from lakes of the Cobalt area in Ontario.

Hot plate digestion. Three tailing samples were used with this method for which 7.3 mL of 15M HNO_3, 1.85 mL of 12M HCl and 1.0 mL of 27.4M HF were added into a Teflon digestion beaker containing 0.5000 g of tailings. Samples were placed into the oven at 80-100 °C for one hour, then in the sand bath at 110-130 °C for three hours with manual stirring from time to time. After the samples were cooled down to room temperature, 1.5 g of H_3BO_3 was added and all samples were stirred for 30 min. Samples were fixed to 25.00 mL with DDW, than diluted 100 times with 3.0M HCl. The samples were analyzed for Te determination using HG-AFS.

Microwave digestion.

(1) Digestion temperature: 0.5000 g of tailing samples were precisely weighed and transferred into a Teflon digestion vial with 10.0 mL of *aqua regia* (2.5 mL of 15.0M HNO_3 + 7.5 mL of 12.0M HCl). The samples were treated in the microwave digestion system from room temperature to 85 °C in 5 min, from 85 °C to different test points starting from 120 to 220 ^oC in 7 min, left at the test point temperature for 20 min and then let to cool down for 20 min before

being placed in an icy bath. When samples reached room temperature, they were diluted 10 times then added the appropriate amount of thiourea to have a concentration of 0.25% (w/v) in the final solution. The digest was fixed to 25.00 mL. The sample was then diluted 100 times with 3.0M HCl. The samples were analyzed for total Te using HG-AFS.

(2) Proportions of digestion reagents: To determine the best digestion conditions, approximately 0.5000 g of tailing sample was weighed precisely and added to different volumes of concentrated acids and were transferred to Teflon digestion vial (Table 2-2). After the microwave digestion was done and the sample cooled, boric acid was added to neutralize HF. The samples were fixed to 25.00 mL with DDW. After an appropriate dilution with 3.0M HCl, the sample was analyzed using HG-AFS. Standard additions of Te(IV) to the digestion matrix were performed to validate the method and also investigate whether there was any interference caused by the digestion matrix.

Table 2-2 Digestion reagents

Digestion ID	Sample weight/g	Mass of boric acid/g	27M HF /mL	15M HNO_3 /mL	12M HCl /mL
D#1	0.5004	1.500	2.0	7.3	1.9
D#2	0.5002	0.750	1.0	2.0	5.0
D#3	0.5007	0.400	0.5	5.0	2.5
D#4	0.5010	0.400	0.5	3.0	5.0

The microwave digestion system that was used to the following experiments is: from room temperature to 85 °C in 5 min, from 85 °C to 220 ^{o}C in 7 min, left at 180 °C for 20 min and then let it vent for 20 min to reduce the pressure.

2.8. Test of Te (VI) reduction using the microwave digestion system

The objective of this experiment was to test if Te(VI) could be reduced using the D#1 digestion system (2.0 mL HF, 7.3 mL HNO_3, 1.9 mL HCl). Two groups of samples were prepared. Group one contained 100 µg/L Te (IV) and D#1 reagents; and Group two containing 100 µg/L Te(VI) and D#1 reagents. Both samples were subjected to the microwave treatment

and 1.5g of boric acid was added and the solution was stirred for 30min. The sample were transferred into a pre-cleaned 50.0 mL polypropylene centrifuge tube after having been thoroughly cooled in an icy bath and fixed to 25.00 mL with DDW. The sample were diluted 100 times with 3.0M HCl and analyzed for Te using HG-AFS.

2.9 Digestion of certified reference material (CRM)

For method validation, the certified reference material GBW07312 with a total Te concentration of 0.30 ± 0.07 μg/g was analyzed. It is an aquatic sedimentary sample, produced by the Chinese National Standard Material Bureau. Due to the rareness of certified materials for Te, the method development work was also conducted with other type of samples. A mass of 0.5000 g of the (CRM) was precisely weighed and transferred into a Teflon digestion vial, the D#1 reagents were added to the weighed samples and then the digestion vials were closed tightly and placed into the microwave digestion system. When digestion was done the digestion assembly were put in an icy bath for one hour, then 1.5g of boric acid was added to the samples in the vials, and solution were stirred for 30 min. Finally the sample solution in digestion vials was transferred into a pre-cleaned 50.0 mL polypropylene centrifuge tube and fixed to 50.0mL with DDW. The samples were diluted 40 times with 3.0M HCl and total Te was analyzed using HG-AFS.

2.10. Digestion method for environmental samples

Several environmental samples were used in this study. Tailing samples were collected from the Vale tailing site on September 27, 2011. Except for sample Tail. #ISP, a deeply oxidized surface tailing sample (sulfur 2.8%), other samples were considered original tailing samples containing a high concentration of sulfur (30 – 36%). Two sediment samples from Clearwater Lake and McFarlane Lake (collected in 2006 and kept at -80 °C) were analyzed. The third group of samples was collected from Cobalt Lake and Crosswise Lake in the Cobalt area, Ontario. There was no sulfide in these sediment samples; instead they contain significant amounts of carbonates and high arsenic levels. Although they were all inorganic samples, their major chemical composition were quite different. Those sediments and tailings were digested following the established procedure D#1 and sample weight was always approximately 0.5000 g.

Chapter 3

3. Results and Discussion

In this Chapter, the experimental results are presented along with the corresponding discussions.

3.1 Optimal instrumentation and measurement conditions

3.1.1 Lamp current (mA)

Any hollow cathode lamp or boosted hollow cathode lamp used in atomic adsorption and atomic fluorescence emission has a certain lifetime. The selection of its optimal operating condition does not only affect its lifetime but also the sensitivity of the analysis.

Table 3-1 shows the best signal that could be obtain from the lamp to detect Te (IV) using HG-AFS. The best signal obtained was at a primary power of 15 mA and a boost of 15.7 mA. These setting have been used to perform all the experimental work presented in this thesis.

Table 3-1 Study on optimal lamp current for a Te solution of 60 µg/L.

Primary (mA)	10.0	11.1	12.2	13.3	14.4	**15.0**	15.0	15.0
Boost (mA)	10.8	12.0	13.1	14.3	15.5	**15.7**	16.2	17.5
Te (IV) Peak Height	10.0	14.4	24.1	32.4	46.0	**71.2**	69.3	55.8

3.1.2 Effect of hydrochloric acid concentration on the analytical signal

Different concentrations of HCl were used to determine the best conditions of acidity to react with the borohydride solution and analyze Te element using HG-AFS. As illustrated in Figure 3-1, a 3.0M concentration of HCl was determined as the best acidity for Te determination using HG-AFS.

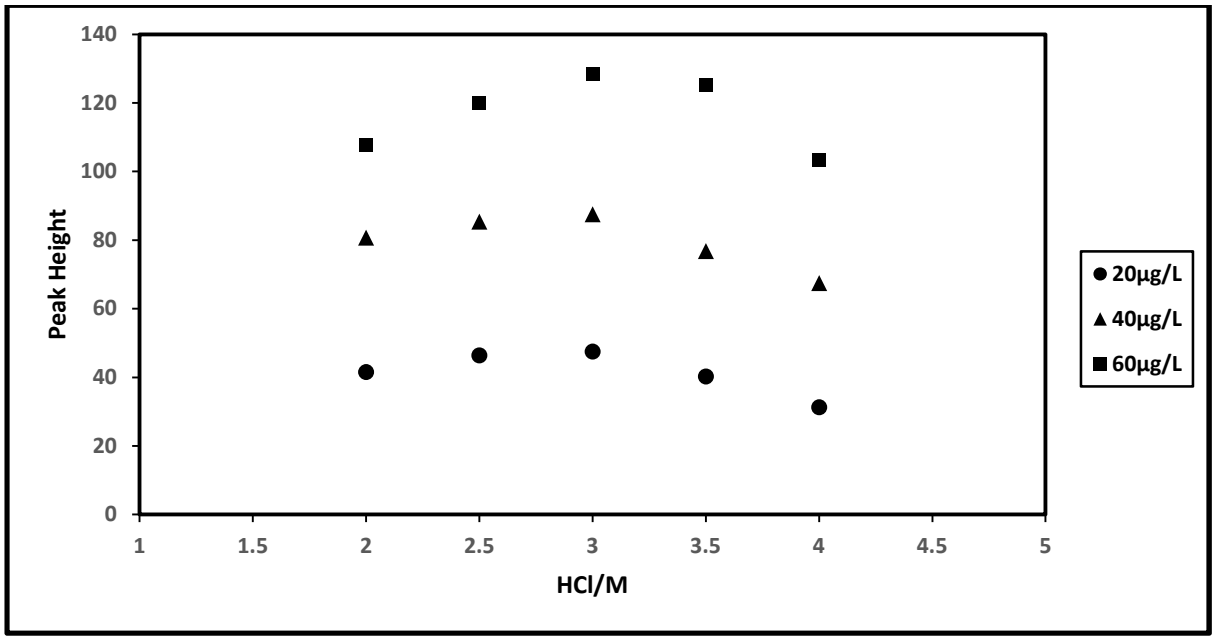

Figure 3-1. Effect of HCl molarity on 20, 40 and 60 µg/L Te (IV) solution signal (15 mA primary, 15.7 mA boost of the lamp)

3.1.3 Detection limit of Tellurium by PSA 10.055 Millennium Excalibur

Figure 3-2 shows the lowest value of Te(IV) that could be detected using HG-AFS. As indicated by the figure, the signal produced by a 50 ng/L solution is very close to the background noise produced by the blank solution. Considering also the instrumental variations, the detection limit of Te by this instrument was therefore estimated at around 150 ng/L or three times the value of the lowest signal close to blank. Although in their earlier advertisement, PSA claimed a detection limit of 10 ng/L for Te, our results show that detection limit for quantification should be much higher than the claimed value.

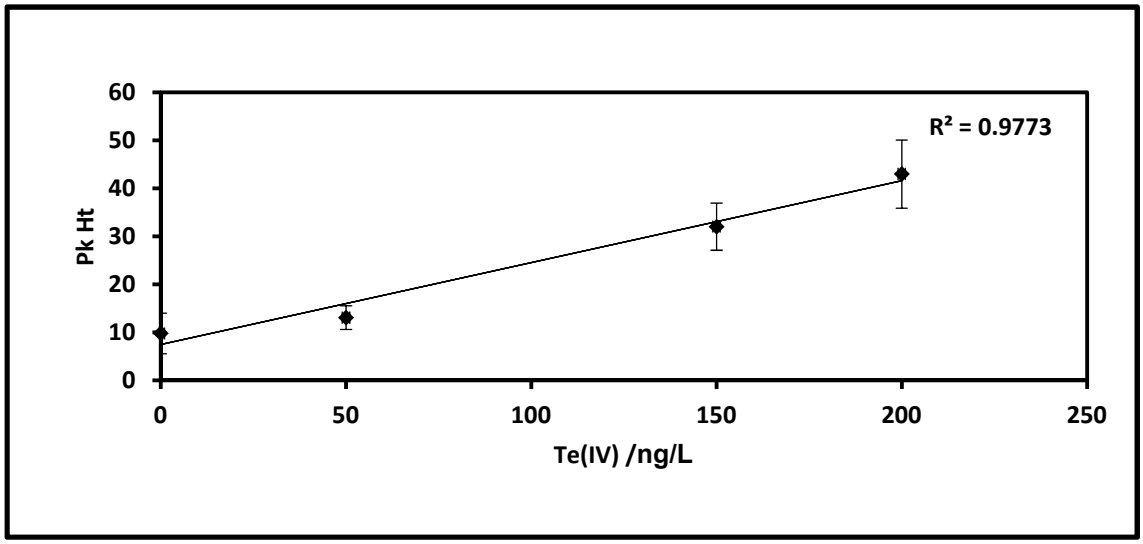

Figure 3-2. Detection limit of Te(IV) by PSA10.055 Millennium Excalibur.

3.1.4 Study on the linearity range of tellurium by HG-AFS

The linearity of the determination of Te(IV) by HG-AFS in a 3.0M HCl solution was investigated. As indicated by Figure 3-3, the AFS signal remains linear up to 100 µg/L after which it tends to become curved. All solutions exceeding the concentration of 100 µg/L must then be diluted to remain in the linear portion of the calibration.

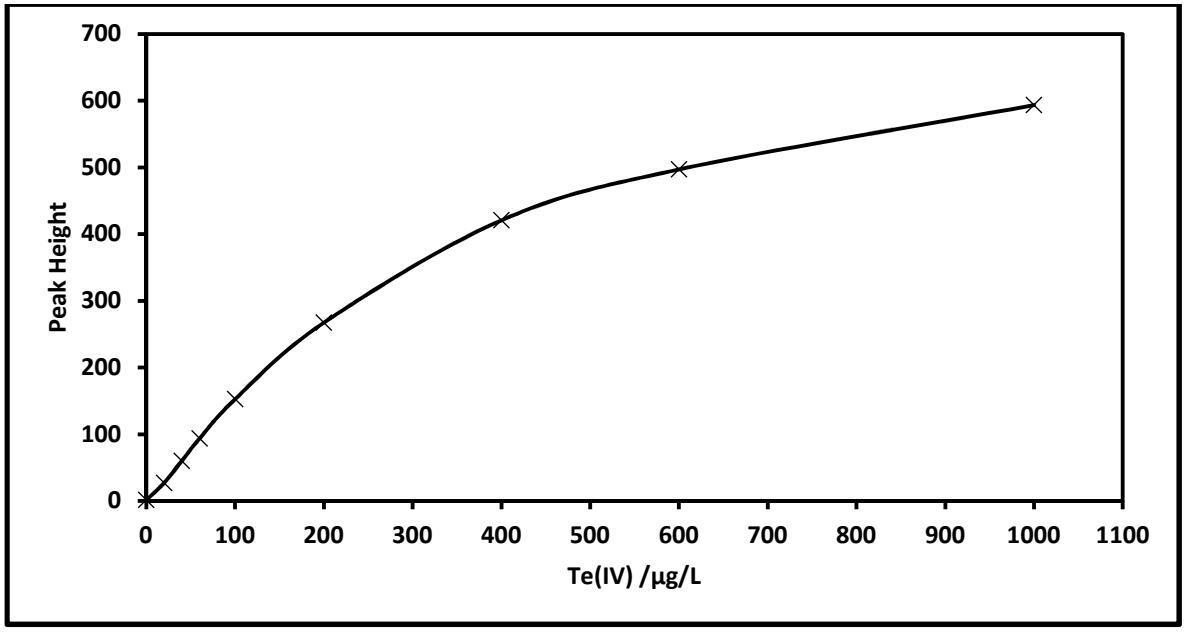

Figure 3-3 Linearity of calibration of Te(IV) in 3.0M HCl as measured by HG-AFS

3.2 Pre-reduction of Te(VI) to Te(IV)

As it has been mentioned in the Introduction, Te(VI) cannot form H_2Te without previously being converted to Te(IV). To be able to determine Te in other valences, a conversion to Te(IV) is therefore needed. In most geological and biological samples, sample digestion with strong acids under high temperatures is needed, which would be very likely to bring Te to its higher valence of 6, therefore a pre-reduction of Te(VI) to Te(IV) is essential.

Some commonly used reducing reagents were tested at room temperature with a maximum concentration of 0.602M for KI, 0.420M for KBr, 0.284M for ascorbic acid and 0.555M for oxalic acid in a solution that contained 60 µg/L of Te(VI) and 3.0M HCl. These solutions were set on the counter for 24 h and the Te concentration was determined. It was found that Te(VI) was not efficiently converted to Te(IV) in all chemical systems above-mentioned.

Also, in 3.0M HCl with the microwave treatment at a temperature of 110 ^{o}C did not reduce Te(VI) to Te(IV) and it was suspected that temperature could be not high enough. Prior to testing higher temperatures, the possible volatility of Te compounds was investigated.

3.2.1 Study on the volatility of tellurium in HCl matrix under microwave conditions

Under a high temperature, several metals and metalloids such as lead, selenium and zinc tend to form volatile compound when chloride ions are present in solution. Since a relatively high concentration of HCl 3.0M and high temperature (110^{o}C) were used in pre-reduction tests with the microwave oven, it was necessary to evaluate the potential loss of Te during the sample digestion and manipulation.

The results from the Group One test (see details in section 2.4.1) showed a gradual increase in recovery, from 83 to 104 % (Figure 3-4a), whereas results from the Group Two test demonstrated a constant recovery of nearly 100% (Figure 3-4 b). Because in the Group One test, the solution in each digestion vial was not previously cooled down before transfer, the temperature in the solution was still relatively high when the first vial was opened and a noticeable amount of Te was lost, probably in the gaseous form of $TeCl_2$. The temperature of the solution in the second and other vials become lower and the loss of volatile Te became lower, consequently improving the recovery of Te(IV) in solution (Figure 3-4a). Since the solutions in

the Group Two test were previously cooled down before transfer, the loss of Te(IV) was insignificant.

Considering the formation of volatile Te and its potential loss under high HCl and temperature conditions, it is necessary to transfer a digested solution when it was thoroughly cooled down. The cooling of digestion segments was therefore practiced in all our microwave digestion treatments.

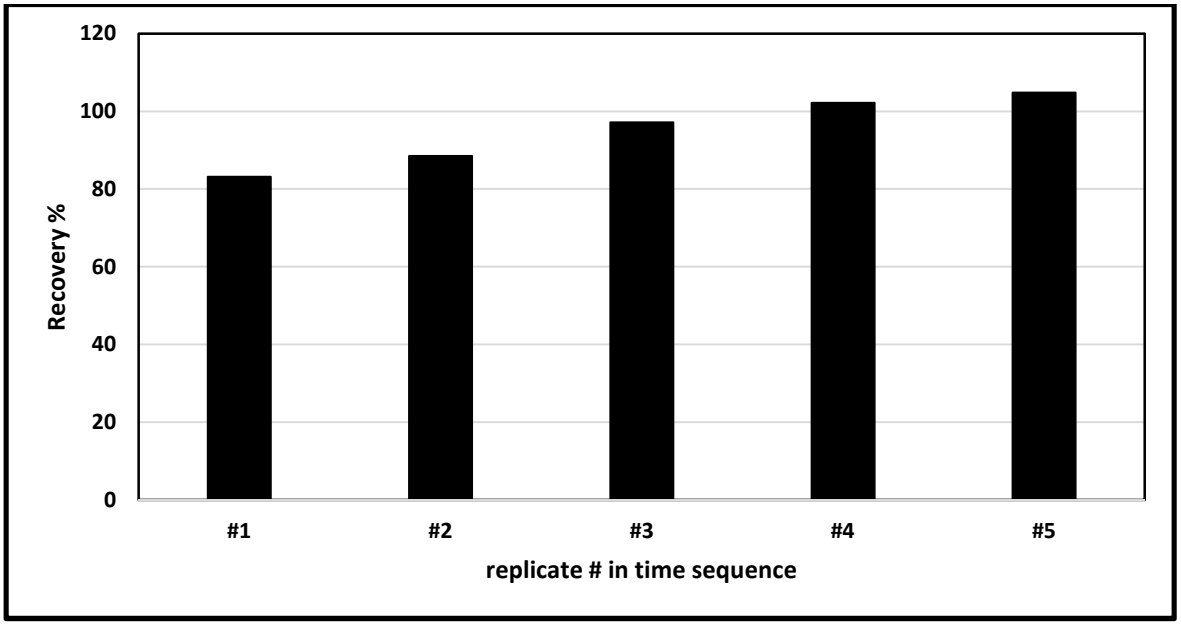

Figure 3-4 (A) Tested solutions containing 10 µg/L Te(IV) in presence of 3.0M HCl.

The solutions in Group One Test were transferred before they were thoroughly cooled down.

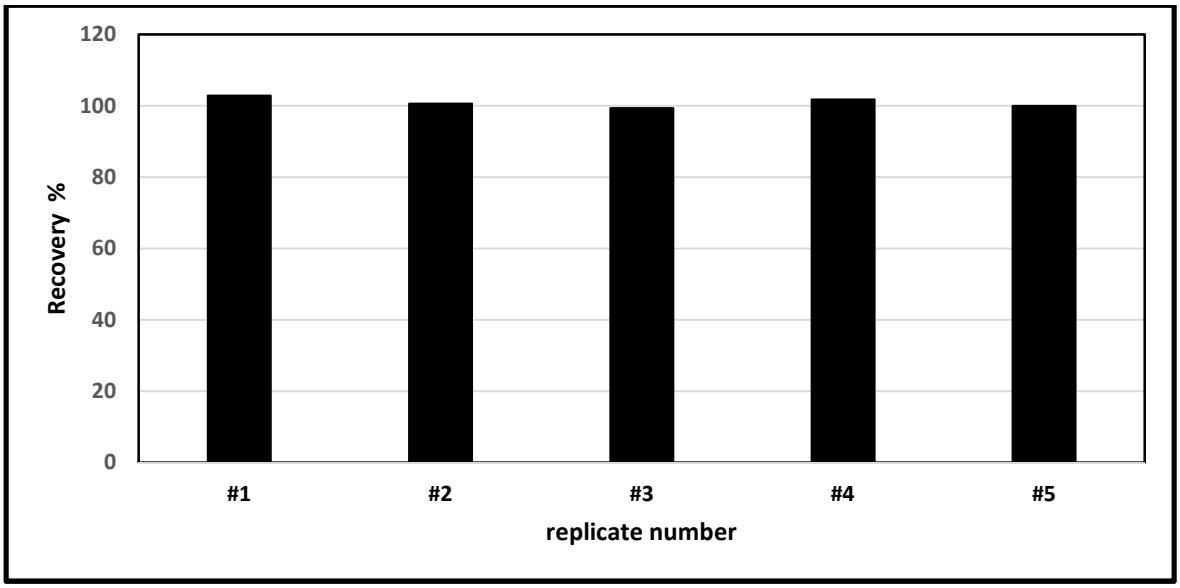

Figure 3-4 (B) Tested solutions containing 10 µg/L Te(IV) in presence of 3.0M HCl.

The solutions in Group Two Test were transferred after they were completely cooled.

3.2.2 KBr as reducing agent

The utilization of the 3.0M HCl solution at 110 °C was inefficient to reduce Te(VI) to Te(IV). Therefore, KBr was tested as reducing agent. As shown in Figure 3-5, a 0.17M KBr solution proved to be a good reducing agent with almost 100% reduction of Te (VI); the figure also shows that KBr does not interfere with the Te(IV) signal because the two linear correlations using Te(VI) or Te(IV) are almost identical.

Most of the experiments in this section were done with a 10 µg/L or less Te(IV) solution, to determine the right amount of KBr needed to reduce 10 µg/L of Te(VI). Several concentrations of KBr were prepared. As indicated in Figure 3-6, the recovery of Te(VI) increased up to a concentration of 0.17M in the solution with a 98% recovery. The addition of more KBr did not affect the reduction because almost all Te(VI) had already been transformed to Te(IV). However, it was necessary to test another reducing agent because the digestion of tailings and sediments in presence of *aqua regia* lead to the formation of bromine in solution and to the creation of a major interference in the analytical process as it expressed in the reaction

below:

$$4H^+ + 2\,NO_3^- + 2\,Br^- \longrightarrow 2\,NO_2\,(g) + Br_2 + 2H_2O$$

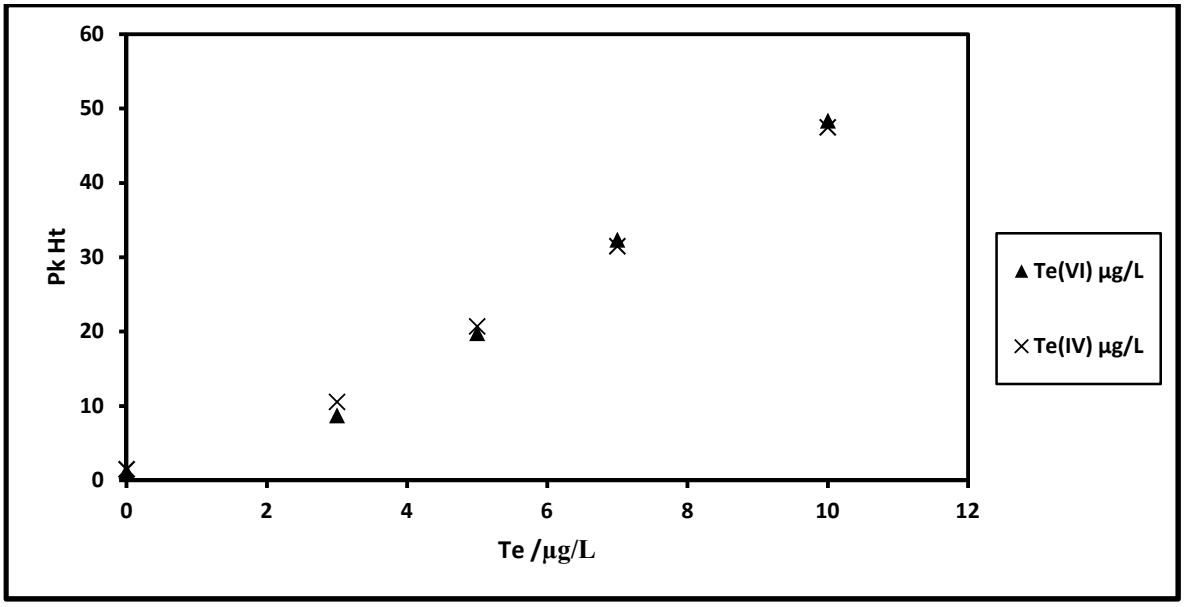

Figure 3-5 Pre-reduction of Te(VI) in presence of 0.17M KBr under microwave treatment at 110 ^{o}C and comparison with a standard Te(IV) calibration curve.

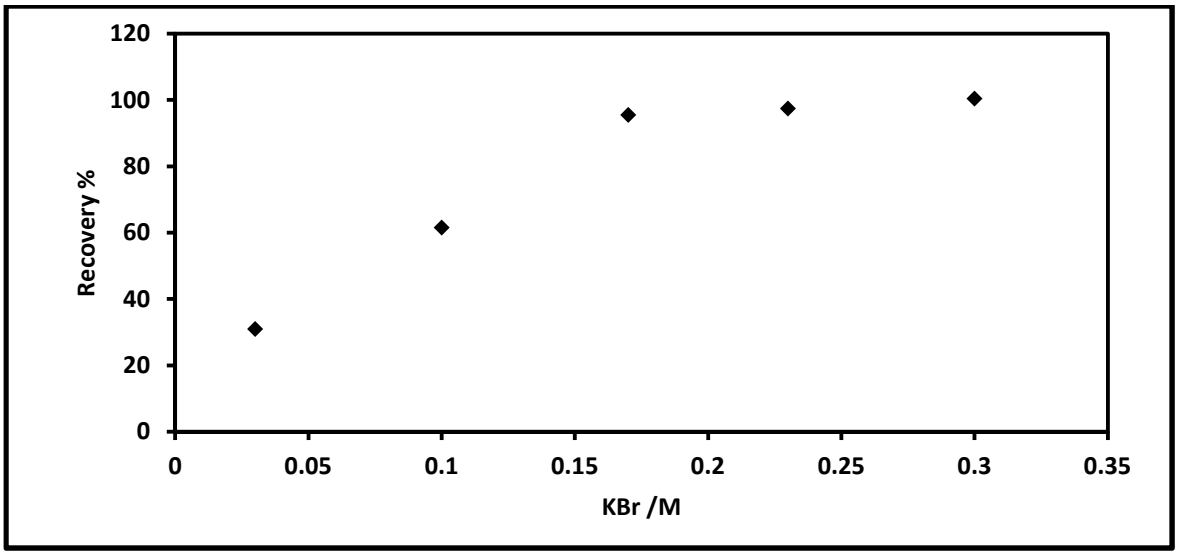

Figure 3-6 Concentration effect of KBr on the reduction of a 10µg/L Te(VI) solution.

3.2.3 Pre-reduction using different concentrations of HCl

To replace KBr, it was then decided to test higher concentrations of HCl as a reducing agent. Table 3-2 shows that at 110 ^{o}C in the microwave treatment, using 3.0M HCl could only lead to a 22% recovery of Te(VI); the recovery increased to 71% with 4.0M HCl, and Te(VI) was successfully completely reduced and recovered as Te(IV) in 5.0M HCl

Table 3-2 Effect of HCl concentration on Te(VI) pre-reduction.

HCl conc. (M)	Added Te(VI) /µg/L	Measured Te(VI) /µg/L	Recovery %
3.0	10.00	2.25	22.5
4.0	10.00	7.19	71.9
5.0	10.00	10.81	**108.2**

Hence 5.0M HCl and 110 ^{o}C microwave treatment were the adopted conditions to reduce Te(VI) into Te(IV) in future determinations.

3.3 Interference from metal ions on the Te(IV) signal

Tellurium is one of the rarest elements of the Earth's crust and because most natural environmental samples are very complex, it is necessary to test for possible interfering elements when measuring Te using HG-AFS. A series of tests was designed to study the effect of other elements present in solution on the determination of Te(IV). Figure 3-7 indicates that Ni (II), Pb (II), Fe(III), Co (II) and Cr (VI) do not cause serious interference with Te determination at concentrations lower than 1000 µg/L in solution. A 100% Te (IV) signal could be obtained with up to 10 mg/L Pb (II) and 1.0 mg/L with the other three elements. Figure 3-8 reveals that Zn (II), Cr(III) and Mo(VI) caused no interference in the determination of Te (IV) but Mn (II) slightly interfered. Finally, it was noticed in Figure 3-9 that Cu (II) could severely reduce the signal of Te (IV) with a visible interference starting at as low as 10 µg/L. This may be due the formation of a copper telluride complex (Bye et al, 1984).

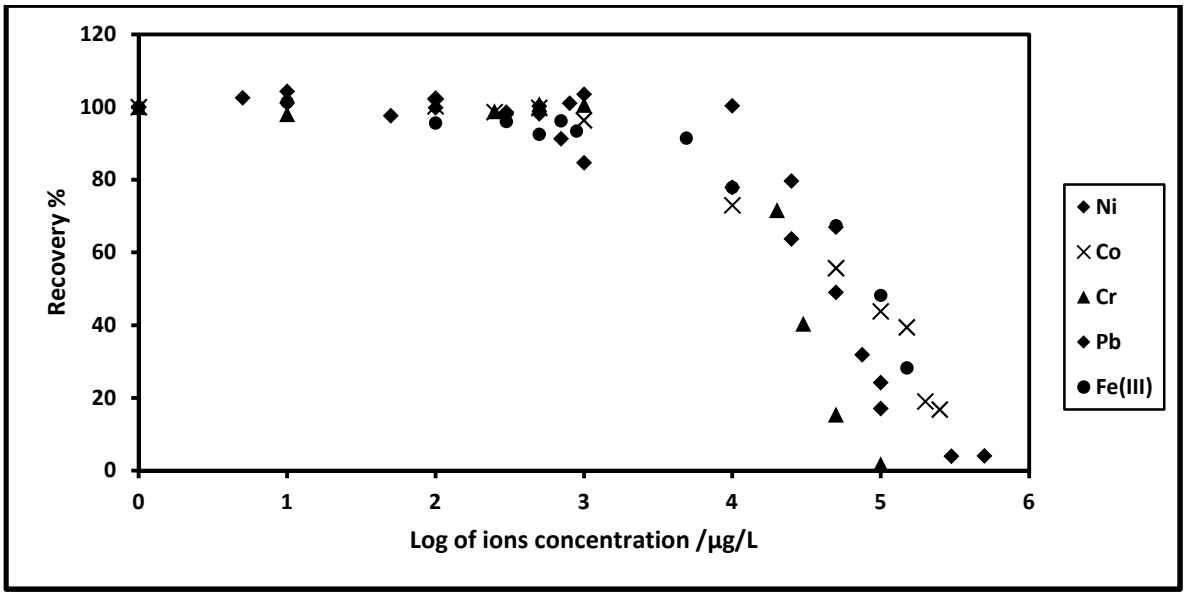

Figure 3-7. Study of Ni(II), Co(II), Cr(VI), Fe(III) and Pb(II) interference on a 10 µg/L Te(IV) solution in 3.0M HCl.

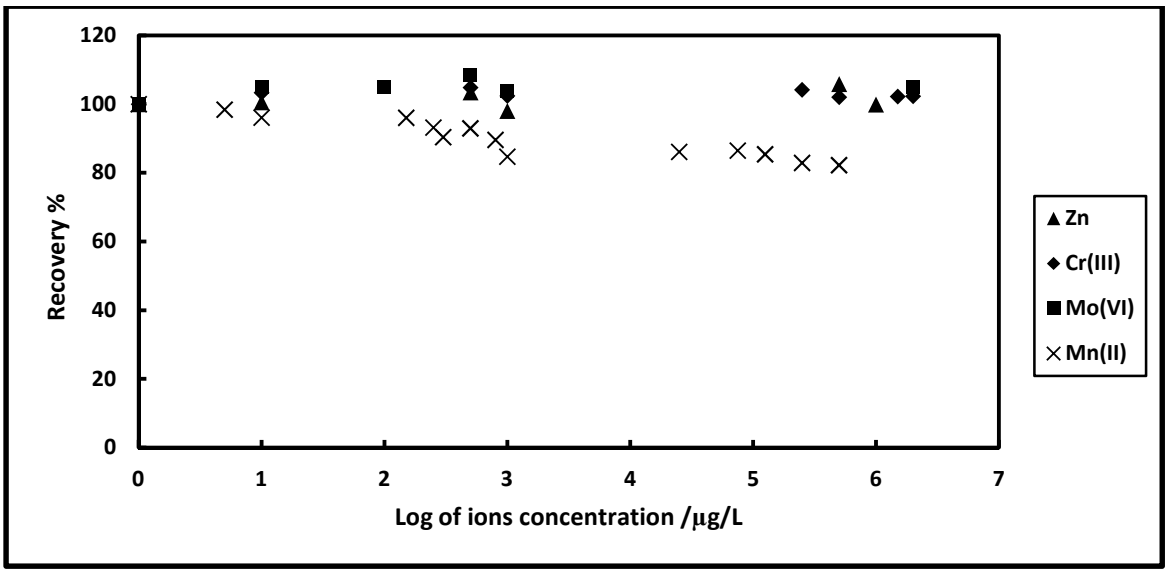

Figure 3-8. Study of Zn(II), Cr (III), Mo(VI) and Mn(II) interference on a 10 µg/L Te (IV) solution in 3.0M HCl.

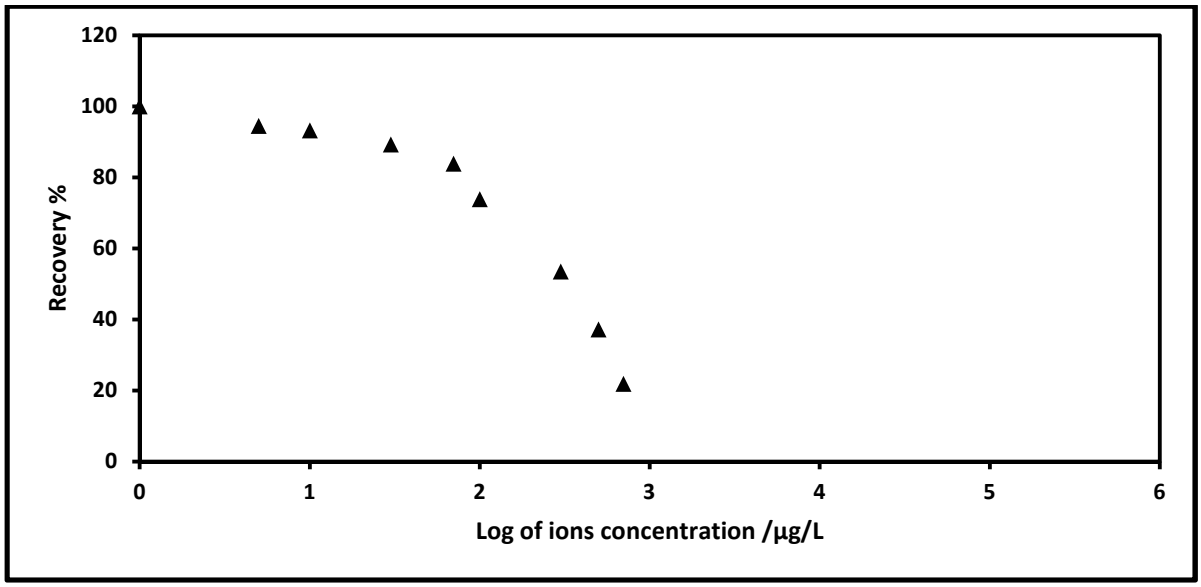

Figure 3-9. Study of Cu(II) interference on a 10 µg/L Te (IV) solution in 3.0M HCl.

3.4 Selection of masking agents

From the results of the tests described above, it was found that the majority of other elements do not cause significant interference to Te(IV) measurement until they reach high concentrations or do not cause any interference at all. Only Cu(II) was proved to cause severe negative interference at a concentration as low as a few µg/L. Thus, the effort was made to find a masking agent that could eliminate that interference. Diluted solutions of thiourea, L-cysteine, L-ascorbic acid and 1,10-phenanthroline were tested on a 10µg/L Te(IV) solution. The results presented in Table 3.3 clearly indicate that the 0.25% (w/v) thiourea solution could completely control the interference due to the presence of 5 mg/L of Cu(II) in a 3.0M HCl solution.

Table 3-3 Studies of the effectiveness of masking regents on the interference of 5mg/L Cu^{2+} in the determination of a 10 µg/L Te(IV) solution.

Sample ID	8-hydroxy-quinoline 1.0% (w/v)	Thiourea 0.25% (w/v)	L-Cysteine 2.0% (w/v)	L-Ascorbic Acid 2.0% /(w/v)	1,10-Phenan-throline 1.0% (w/v)
Measured Te(IV) µg/L	1.5	10.4	1.8	2.8	3.1
Recovery of Te %	15	104	18	27	31

The masking capacity of 1.0% (w/v) solutions of 1,10-phenanthroline and 8-hydroxyquinoline with different concentrations of Cu^{2+} was studied. In the study, the concentration of Te(IV) was kept constant at 10 µg/L. The study showed that although neither of these two masking agents was very effective, 1,10-phenanthroline was better than 8-hydroxyquinoline at low Cu^{2+} concentration. Their masking capacity dropped drastically when Cu^{2+} was higher than 100µg/L (Figure 3-10).

The 0.25% (w/v) thiourea solution was also tested in detail (Figure 3-11) and the recovery of Te was still at ~83% when the Cu(II) concentration had reached 30.0 mg/L. This is still a good recovery considering that Te concentration is usually very low in most environmental samples. Different concentrations of thiourea were tested to confirm if the Te recovery could be improved when adding more thiourea in the solution but the 0.25% (w/v) ended up being the best choice.

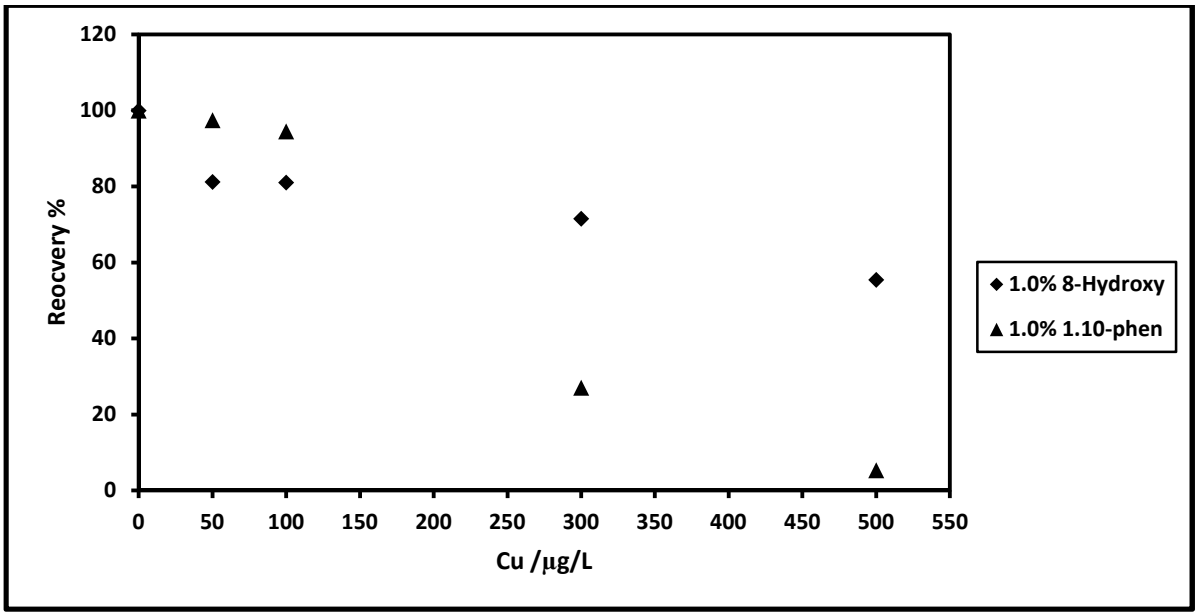

Figure 3-10. Effectiveness of masking agent 1.0 %(w/v) 1,10-phenanthroline and 1.0 % (w/v) 8-hydroxyquinoleine in 3.0M HCl solution on the determination of 10 µg/L Te(IV).

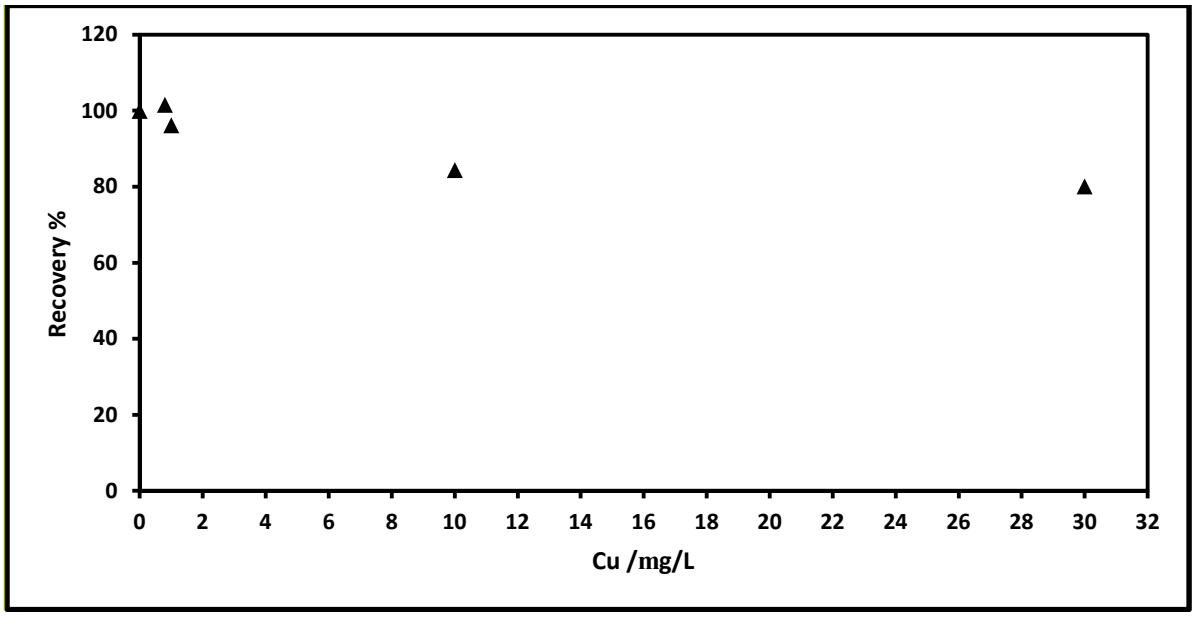

Figure 3-11 Effectiveness of masking agent 0.25%(w/v) thiourea in 3.0M HCl solution on the determination of 10 µg/L Te(IV).

To further test the masking capacity of thiourea, different concentrations of mixed metal ions of Cu(II), Cr(VI), Cr(III), Fe(III), Zn, Cr(III), Mn(II), Mo(VI) and Ni(II) were prepared with the presence of 10 µg/L of Te(IV) and 0.25%(w/v) thiourea in each sample solution. The results are-presented on Figure 3-12; the recovery of Te(IV) was around 100% up to 10 mg/L and then it dropped to 50% when the mixed metal ions reached 25 mg/L of each metal. The results show that thiourea is a very effective masking agent for an analytical system that contains high level of transition metals. The data also show that a thiourea concentration of 0.25%(w/v) should be sufficient to be used to remove interferences for most sample analysis.

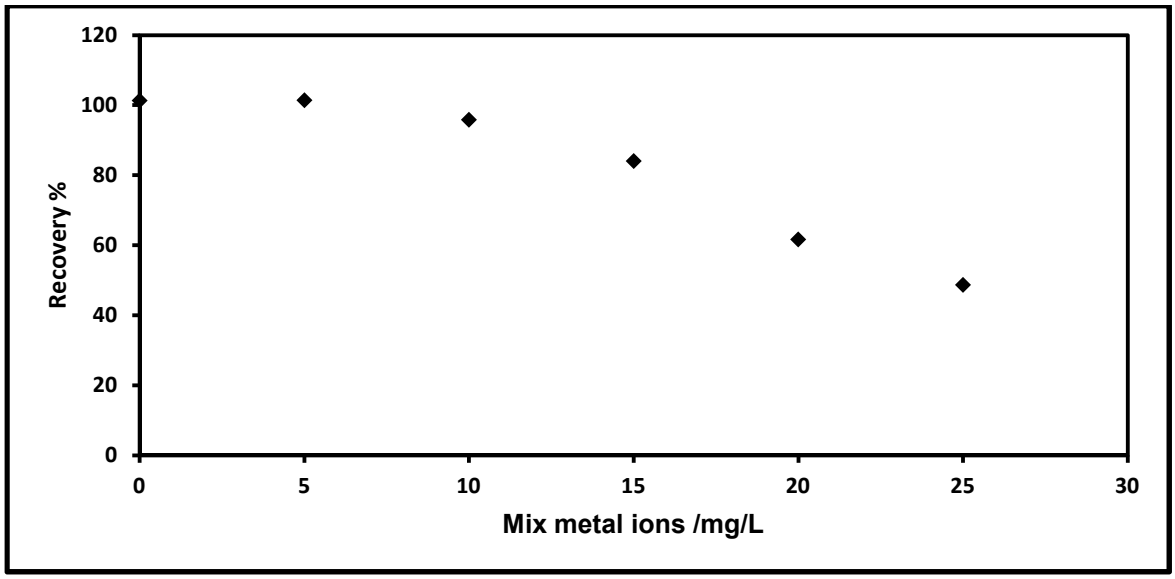

Figure 3-12. Effect of the mixture of different element ions Cu(II), Cr(VI), Cr(III), Fe(III), Zn, Co(II), Mn(II), Mo(VI) and Ni(II) on the recovery of 10µg/L Te(IV) in presence of 0.25%(w/v) thiourea.

3.5. Tellurium in Sudbury Lake waters

Water samples collected from Ramsey Lake (RL) and Kelly Lake (KL) were analyzed in the presence of 0.25%(w/v) thiourea masking agent and no Te was detected in these two samples. Therefore, water samples were spiked with known amounts of Te(IV) and Te(VI) to confirm the method. As indicated by data presented in Table 3-4, the recovery of Te(IV) was very good.

Table 3-4 Recovery of spiked Te (IV) in Kelly and Ramsey Lakes (KL and RL) water samples.

Sample ID	Spiked Te(IV) /µg/L	Measured Te(IV) /µg/L	Recovery %
KL0	0.00	ND	N/A
KL1	3.00	3.21	**107**
KL2	5.00	5.07	**101**
KL3	7.00	7.34	**104**
KL4	9.00	9.79	**108**
RL0	ND	ND	N/A
RL1	5.00	5.40	**108**
RL2	15.00	14.66	**97**
RL3	20.00	20.89	**104**

ND: not detected; N/A: not applicable

To determine Te(VI) in the two lake samples, the samples were first spiked with a Te(VI) standard solution, then these solutions were subjected to a pre-reduction in 5.0M HCl at 120 ^{o}C in a microwave oven as described in section 2.6. The results are given in Table 3-5.

The results showed that in both lake surface water, the concentrations of Te(IV) and Te(VI) were below the detection limit of this instrument. However, the recovery of the spiked Te(IV) and Te(VI) are both very satisfactory.

Table 3-5 Recovery of spiked Te (VI) in Kelly and Ramsey Lakes (KL and RL) water samples after pre-reduction.

Sample ID	Spiked Te(VI) /µg/L	Measured Te(VI) /µg/L	Recovery %
K L0	0.00	ND	N/A
KL1	3.00	3.15	**105**
KL2	5.00	4.72	**94**
KL3	9.00	9.28	**103**
RL0	0.00	ND	N/A
RL1	3.00	3.16	**105**
RL2	5.00	4.84	**96**
RL3	9.00	8.50	**94**

ND: not detected; N/A: not applicable

3.6. Digestion method for tailings and sediments.

3.6.1. Hot plate digestion method: Three tailing samples were digested using the hot plate digestion process described in section 2.7. Data in Table 3-6 show that tailing number 1 contained more Te than the other tailing samples. Also that sample did not get digested completely and it was possible to observe some small solid particles at the bottom of the digestion tubes; this could be some resistant alumino-silicates in the sample and it would affect the recovery of Te.

Table 3-6 Digestion of tailing samples using the hot plate method.

Sample ID	Measured Te /µg/g
Tail#1	10.41
Tail#3	5.29
Tail#5	2.75

3.6.2. Microwave digestion system: Digestion temperature: one of the important factors that can help to digest solid samples is the temperature. Therefore, it is important to know the optimum conditions to design the microwave digestion system steps. It can be observed clearly from Figure 3-13 that the extraction of Te from the tailing samples gradually got higher up to a temperature of 180 ^{o}C, then started to drop. This is possibly caused by the loss of Te in volatile forms by leakage during the digestion step at temperatures higher than 180 ^{o}C. Therefore, 180 ^{o}C was chosen as optimal temperature for sample digestion. A summary of the temperature program used in the microwave digestion program in presented in Figure 3-14.

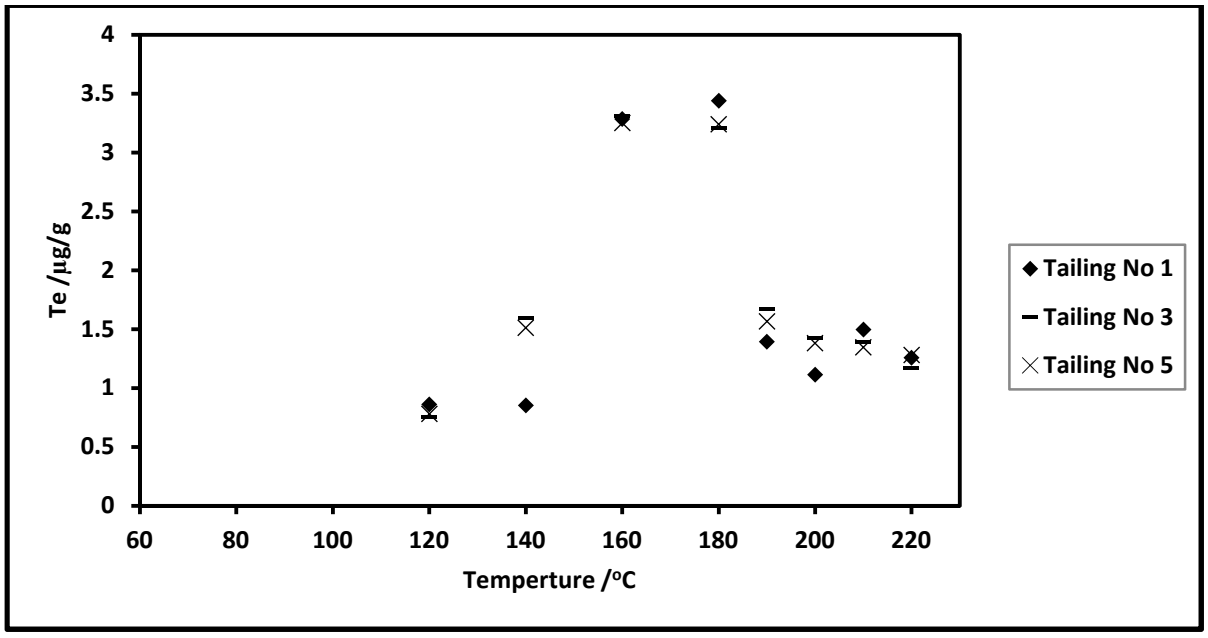

Figure 3-13 Digestion of tailings under different temperatures using the microwave system. The final solution concentration was 3.0M HCl.

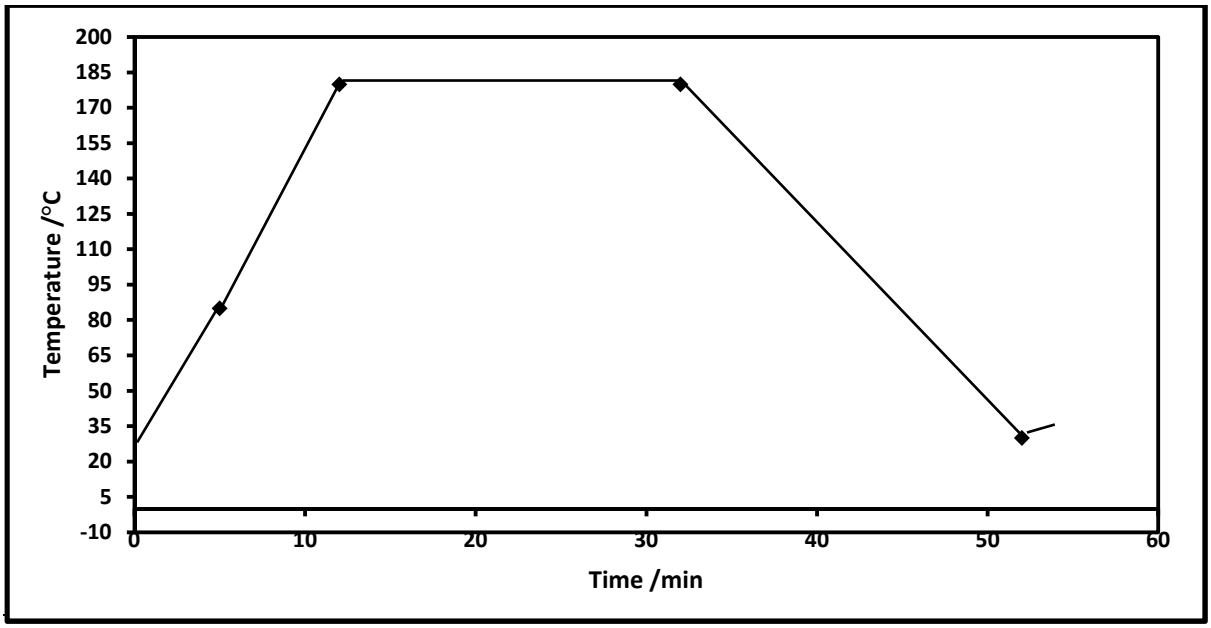

Figure 3-14 Summary of the microwave digestion program in 3.0M HCl.

3.6.3. Digestion Regents: Four different combinations of reagents were used to digest tailing sample#3 as described in Table 3-7 below. The goal was to find the best digestion system for the solid environmental samples.

Table 3-7 Tested digestion reagents for tailing sample.

Digestion ID	Sample weight /g	27M HF /mL	15M HNO_3 /mL	12M HCl /mL	Boric acid /g
D#1	**0.5003**	**2.0**	**7.3**	**1.9**	**0.7500**
D#2	0.5005	1.0	2.0	5.0	0.7500
D#3	0.5007	0.5	5.0	2.5	0.4000
D#4	0.5001	0.5	3.0	5.0	0.4000

Table 3-8 shows that the D#1 digestion system produced the highest total Te value. The efficiency maybe due to the high concentration of HF acid to digest silica in the sample and the high concentration of nitric acid to break chemical bonds and free all Te ions from the sample.

Table 3-8 Total Te measured in tailing # 3 digested in 4 different digestion systems (N=3).

Sample ID	Average Te /µg/L	SD /µg/L	RSD %
D#1	**23.96**	0.35	1.47
D#2	17.37	0.38	2.17
D#3	20.54	1.39	6.79
D#4	19.22	0.12	0.63

3.6.4 Test on the effect of D#1 digestion system to chemical valence of Te(IV) and Te(VI)

The objective of this experiment was to confirm whether Te was presented as Te(IV) or Te(VI) in the D#1 digestion system. To achieve this, a small aliquot of standard solution of Te(IV) or Te(VI) was spiked into the microwave digestion vial containing an aliquot of D#1 digestion agents and subjected to a microwave digestion according the program given in Figure 3-15. The digest was transferred into a 25.00 mL volumetric flask and the Te(IV) or Te(VI) concentration in such a solution was at 600 ng/L. The samples were determined in presence of the 0.25%(w/v) thiourea masking agent. The standard addition technique was applied to monitor the matrix effect on the signal. It was found that the slope of the calibration curve prepared in the D#1 matrix had slightly dropped. A triplicate test was performed for both Te(IV) and Te(VI). As indicated by data presented in Table 3-9, the chemical reagents used in the D#1 system do not affect the chemical valence of Te(IV) and any Te(VI) in such digestion condition should be converted to Te(IV), therefore the pre-reduction step is not needed. The test also indicates that even though HNO_3 was a dominant compound in the digestion system, the chemical environment in such a system is not strong enough to oxidize Te(IV) to Te(VI).

Table 3-9 Recovery of spiked Te species subjected to D#1 digestion reagents and at a microwave digestion temperature 180 ^{o}C (N=3).

Sample ID	Recovery %	SD /μg/L
Te(IV) 600ng/L	**93.26**	4.85
Te(VI) 600ng/L	**91.00**	1.52

3.7 Method validation with certified reference material GBW07312.

To validate the digestion and analytical method, the certified reference material GBW07312 was digested following the same procedure and the total Te was measured. The digestion combined reagent was D#1 (2.0 mL of 27M HF, 7.3 mL of 15M HNO_3 and 1.9 mL of 12M HCl). The microwave digestion program included the following steps: from room temperature to 85 °C in 5 min, from 85 °C to 180 ^{o}C in 7 min, left at 180 °C for 20 min and then left cooled for 20 min to reduce the pressure. The digested samples were transferred after being thoroughly cooled. To eliminate the matrix effect, the standard addition technique was applied. The obtained total Te value was 0.45 ± 0.03 μg/g (N=4). The certified value for GBW07312 is 0.30 ± 0.07 μg/g.

It should be mentioned that the very low concentration of total Te in the certified sediment sample makes difficult the accurate determination of Te. Even in presence of the thiourea solution the possibility of spectral interference in this complex matrix cannot be totally excluded. The relatively large gap between the measured value and the certified value can be likely be explained by this fact.

3.8 Determination of total Te in Sediments and tailing samples.

After the method was validated, other sediments and tailing sample were tested to measure the concentration of total Te in each sample using the established method.

Table 3-10 Total Te (µg/g) in tailing samples from Vale's tailing site. The D#1 digestion system was used, with a comparison of two different volumes of HF.

Sample ID	Total Te (1.0 mL HF)	Total Te (2.0 mL HF)
Tailing #2	58.14	**56.26**
Tailing #4	29.14	**33.36**
Tailing #10	61.66	**66.74**
ISP Tailing (oxidized)	13.37	**15.06**

The results of Table 3-10 shows that increased a 2.0 mL volume of HF do not improve significantly the digestion efficiency. Thus 1.0 mL of 27.0M HF should be sufficient to dissolve all silica in the sample and it would limit the amount of boric acid required to neutralize this acid.

Table 3-11 Total Te in sediments samples (N=3).

Sample ID	Average Te /µg/g	SD /µg/g	RSD %
Sediments samples from Sudbury Lakes			
McFarlane Lake	29.48	2.3	7.79
Clearwater Lake	24.26	2	8.10
Sediments samples from Lakes of Cobalt area			
CrA14	3.21	0.72	22.47
CrA25	10.90	1.10	10.09
CrF6	10.70	1.05	9.77
CoA4	3.46	0.48	13.83
CoA6	3.57	0.47	13.13

A larger RSD was obtained when the concentration of Te was lower than 10 µg/g (Table 3-11).

Conclusions

The following conclusions can be drawn concerning the determination of Te in environmental samples with the protocol that was developed in this thesis:

(1) In general, the acidity level that can give the best signal for Te when analyzing it using HG-AFS was a 3.0M HCl solution. The detection limit using HG-AFS was approximately 150 ng/L.

(2) Tellurium is volatile at high temperatures in the presence of a large amount of HCl. Therefore, it is important to let the sample cool down to room temperature after microwave digestion and before transferring it. KBr could be use as a reducing agent to convert Te(VI) to Te(IV) at 100 ^{o}C. However, it severely interferes with the Te signal when it is mixed with nitric acid. The addition of hydroxylamine cannot eliminate this interference. It can be only used for Te(VI) pre-reduction in the absence of high HNO_3 concentrations. In addition, Te(VI) can be reduced to Te(IV) by using a 5.0M HCl solution during the microwave digestion procedure.

(3) Several metals such as Co(II), Cr(III), Cr (VI), Fe(III), Mn(II), Mo(VI), Ni(II), Pb(II) and Zn(II) did not create any significant interference for the determination of Te. However, when the concentration of Cu^{2+} in the matrix was higher than 5 mg/L, it led to significant interference and required the use of a making agent. Several compounds were tested and the thiourea solution ended up being a good and effective masking agent at an optimum concentration of 0.25% (w/v) in solution.

(4) After comparison of a variety of methods to digest lake sediments and mine tailings, it was found that the best digestion matrix was a mixture of the concentrated acids HF (27.0M, 2 mL), HNO_3 (15.0M, 7.3 mL) and HCl (12.0M, 1.9 mL) using a microwave digestion program that consisted of the following steps: 1) room temperature to 85 ^{o}C in 5 min; 2) from 85 ^{o}C to 180 ^{o}C in 7 min; 3) stay at 180 ^{o}C for 20 min and let drop pressure for 20 min before immersion in an ice bath for one hour.

(5) A certified reference material, sediment and tailing samples were successfully digested using the established method and total Te in each sample was measured using HG-AFS.

(6) The new established method can used to determine with acceptable precision and accuracy low concentrations of Te in several types of environmental samples including lake water, sediments and tailings at low cost.

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Appendices

Appendix 1: Instrumental settings.

A-1 The effect of HCl concentration on Te(IV) signal (peak height).

Te(IV) µg/L	2.0M HCl	3.0M HCl	3.5M HCl	4.0M HCl
20.	40.33	47.53	46.45	41.55
40	76.88	87.61	85.44	80.81
60	125.38	128.48	119.91	107.82

A-2 Reduction of Te(VI) to Te(IV) using 0.17M KBr as reducing agent (N=3).

Te(VI) µg/L	Peak Height Average	STD	RSD%
3.0	8.72	0.57	6.53
5.0	19.78	0.79	4.03
7.0	32.36	2.50	7.74
10.0	48.38	2.48	5.14

A-3 Stability of Te (IV) in 0,17M KBr in three days.

Te(IV) µg/L	Peak Height Average	STD	RSD%
3.0	10.55	1.75	16.63
5.0	20.72	1.03	4.97
7.0	31.49	3.09	9.83
10.0	47.46	2.65	5.58

Appendix 2. Interference of metal ions and selection of masking agent.

A-4 Test of interference of Nickel (mg/L). The 10 µg/L of Te(IV) was present in all solutions used in interference study in 3.0M HCl. Te(IV) was added to different concentration of Ni(II) expressed in mg/L.

Sample ID	Te +0.005	Te +0.01	Te+ 0.05	Te +0.10	Te+ 0.30	Te+ 0.50	Te+ 0.70
Pk Ht	78.8	80.1	74.7	76.9	76.0	76.3	70.2
Measured Te (µg/L)	10.48	10.66	9.94	10.24	10.12	10.15	9.34
Recovery%	102	104	97	100	99	99	91

Interference of Ni(II) results (continued):

Sample ID	Te +1	Te +10	Te + 25	Te + 50	Te + 75	Te +5	Te + 100	Te + 500
Pk Ht	64.9	59.6	49.12	37.96	23.84	13,23	3.47	3.03
Measured Te (µg/L)	8.65	7.93	6.55	5.07	3.19	1.83	0.49	0.43
Recovery%	84	77	64	49	31	18	5	4

A-5 Test of interference of Cobalt (mg/L).

Sample ID	Te +0.10	Te +0.25	Te +0.50	Te +1	Te +10	Te +50	Te +100	Te +150	Te +200	Te +250
Pk Ht	65.36	64.23	64.98	62.76	47.65	36.39	28.78	25.94	12.78	11.32
Measured Te (µg/L)	9.79	9.62	9.73	9.39	7.12	5.42	4,27	3.84	1.86	1.64
Recovery%	100	98	99	96	73	55	43	39	19	16

A-6 Test of interference of chromium(VI) (mg/L).

Sample ID	Te +0.01	Te +0.25	Te +0.50	Te +1	Te +20	Te +30	Te +50	Te +100
Pk Ht	56.34	56.44	57.88	57.78	41.08	23.53	9.33	1.68
Measured Te (µg/L)	9.27	9.29	9.53	9.51	6.73	3.80	1.44	0.16
Recovery%	98	98	101	101	71	40	15	2

A-7 Test of interference of lead Pb (mg/L)

Sample ID	Te +0.01	Te +0.10	Te +0.30	Te +0.50	Te +0.80	Te +1	Te +10	Te +25	Te +50	Te +100
Pk Ht	52.60	53.29	51.26	52.15	52.55	53.82	52.16	34.94	31.76	12.79
Measured Te (µg/L)	9.46	9.59	9.22	9.38	9.46	9.69	9.38	7.45	6.27	2.27
Recovery%	101	103	99	100	101	104	100	80	67	24

A-8 Test of interference of Zinc (mg/L)

Sample ID	Te+0.01	Te+0.50	Te+1	Te+500	Te+1000
Pk Ht	63.18	64.87	61.65	66.30	62.60
Measured Te (µg/L)	10.05	10.33	9.79	10.58	9.95
Recovery%	101	103	98	106	100

A-9 Test of interference of Manganese (mg/L).

Sample ID	Te + 0.005	Te +0.01	Te +0.15	Te +0.25	Te +0.30	Te +0.50	Te +0.80
Pk Ht	331.09	323.56	302.58	313.96	304.94	313.26	302.29
Measured Te (µg/L)	9.37	9.16	8.54	8.88	8.61	8.86	8.54
Recovery%	98	96	96	93	90	93	90

Mn interference results (continued):

Sample ID	Te +1	Te +25	Te +75	Te +125	Te +250	Te +500
Pk Ht	286.42	291.09	292.56	288.34	280.46	278.25
Measured Te (µg/L)	8.07	8.21	8.25	8.13	7.90	7.83
Recovery%	85	86	87	85	83	82

A-10 Test of interference of chromium (III) (mg/L).

Sample ID	Te +0.01	Te +0.50	Te +1	Te +250	Te +500	Te +1500	Te +2000
Pk Ht	68.81	69.75	68.19	69.35	67.97	68.06	68.13
Measured Te (µg/L)	10.12	10.26	10.03	10.20	10.00	10.01	10.02
Recovery%	103	105	102	104	102	102	102

A-11 Test of interference of Molybdenum (µg/L).

Sample ID	Te +0.01	Te +0.10	Te +0.50	Te +1	Te +2000
Pk Ht	69.16	69.24	71.39	68.52	69.20
Measured Te(µg/L)	10.39	10.40	10.73	10.29	10.40
Recovery%	105	105	108	104	105

A-12 Test of interference of Iron. (mg/L)

Sample ID	Te +0.01	Te +0.10	Te +0.30	Te +0.50	Te +0.70	Te +0.90
Pk Ht	49.88	47.09	47.28	45.59	47.37	46.01
Measured Te (µg/L)	9.62	9.07	9.11	8.78	9.13	8.86
Recovery%	101	96	96	93	96	93

Interference of iron results (continued):

Sample ID	Te +10	Te +50	Te +100	Te +200
Pk Ht	38.52	33.43	24.19	14.55
Measured Te (µg/L)	7.39	6.39	4.57	2.68
Recovery%	78	67	48	28

A-13 Test of interference of copper (mg/L).

Sample ID	Te +0.005	Te +0.01	Te +0.03	Te +0.07	Te +0.10	Te +0.30	Te +0.50	Te +0.70
Pk Ht	54.51	53.87	51.89	49.14	44.10	33.79	25.54	17.80
Measured Te (µg/L)	10.26	10.12	9.70	9.11	8.02	5.81	4.04	2.37
Recovery%	95	93	89	84	74	54	37	22

A-14 Effect of masking of 1%(w/v) 8-hydroxyquinoline.

Te(IV) /µg/L	Cu(II) µg/L	Peak Height	Te (µg/L) in Cu+10ppbTe + % 8-hydroxyquinoline	Te Recovery% of Cu+Te10/µg/L+ 1% 8-hydroxyquinoline
10	0	39.83	10.00	100.00
10	50	32.80	8.24	81.23
10	100	32.73	8.22	81.05
10	300	29.15	7.25	71.49
10	500	23.14	6.62	55.43

A-15 Effect of masking of 1%(w/v) 1,10-phenanthroline.

Te(IV) / µg/L	Cu(II) µg/L	Peak Height	Te (µg/L) in Cu + Te10/µg/L+ 1% 1,10-Phenanthroline	Te Recovery%
10	0	31.00	9.80	100.0
10	0.5	30.27	9.55	97.4
10	1	29.44	9.26	94.5
10	10	9.18	2.40	23.5
10	20	6.44	1.36	13.9
10	30	5.13	0.97	9.96

A-16 Effect of masking agent of 0.25%(w/v) thiourea.

Te(IV) /(μg/L)	Cu (μg/L)	Peak Height	Te in, (μg/L) Cu+Te10/μg/L+0.25% thiourea	Te Recovery%
10	0	21.60	9.72	97.16
10	0.5	19.76	8.80	90.54
10	0.8	21.91	9.87	101.59
10	1	20.86	9.35	96.23
10	10	18.57	8.21	84.45
10	30	17.72	7.78	80.10

A-17 Effect of mixture of different element ions [Cu(II), Cr(VI), Cr(III), Ni(II), Fe(III), Zn(II), Co(II), Mn(II) and Mo(VI)]

Te(IV) /μg/L	Ions Mix / mg/L	Peak Height	Measured Te(VI) /μg/L+0.25% thiourea	Te(VI) Recovery%
10	0	34.78	10	100
10	5	35.24	10.27	101.4
10	10	33.38	9.71	95.9
10	15	29.38	8.51	84.0
10	20	21.81	6.24	61.6
10	25	17.45	4.93	48.7

A-18 Spiked Te(IV) recovery from Kelly and Ramsey Lakes water samples.

Sample ID	Spiked Te µg/L	Peak Height	Measured Te /µg/L	Recovery %
K1 blk	NA	5.74	NA	NA
K1	3	20.02	3.21	107
K2	5	29.96	5.07	101
K3	7	42.07	7.34	104
K4	9	55.21	9.79	108
R1 blk	NA	2.73	NA	NA
R1	5	13.66	5.40	108
R2	15	33.36	14.66	97
R3	20	46.6	20.89	104

A-19 Spiked Te(VI) recovery from Kelly and Ramsey Lakes water samples.

Sample ID	Spiked Te (VI) µg/L	Peak Height	Measured Te (VI) µg/L	Recovery %
K1 blk	0.0	4.62	0.0	NA
K1	3	15.53	3.15	105
K2	5	21.81	4.72	94
K4	9	40.16	9.28	103
R1 blk	0.0	5.37	0.0	NA
R1	3	15.58	3.16	105
R2	5	22.29	4.84	96
R3	9	36.96	8.50	94

Appendix 3. Digestion determination method.

A-20 Digestion Temperature: three tailings were used. They were collected from the Vale tailing site; 0.5000g of each sample was weighed and a microwave digestion was used on the samples. The digestion reagent was *aqua regia* (2.5 mL of 15.0M HNO_3 + 7.5 mL of 12.0M HCl). The final acidity of the sample after the dilution was 3.0M HCl.

Temperature °C	120	140	160	180	190	200	210	220
Tail #1/µg/g	0.86	0.85	3.29	3.44	1.39	1.12	1.50	1.26
Tail.#3/µg/g	0.75	1.60	3.31	3.21	1.67	1.43	1.39	1.18
Tail #5/µg/g	0.78	1.51	3.25	3.24	1.57	1.38	1.35	1.28

A-21 Proportions of digestion reagents: tailing number 3 was used to perform this test; approximately 0.5000 g of the sample was weighed and microwave was used for the digestion process. Four digestion reagents were tested Table (2-2), and the final concentration of the 25.00 mL solution was 3.0M HCl.

Digestion ID	**Pk Ht**	**Te /µg/g**
Dig 1. spl#1	37.57	23.90
Dig 1. spl#2	37.16	23.64
Dig 1. spl#3	38.27	24.34
Dig 2. spl#1	26.36	17.66
Dig 2. spl#2	26.10	17.49
Dig 2. spl#3	25.25	16.94
Dig 3. spl#1	33.29	22.14
Dig 3. spl#2	29.38	19.61
Dig 3. spl#3	29.77	19.86
Dig 4. spl#1	29.50	19.21
Dig 4. spl#2	29.31	19.09
Dig 4. spl#3	29.70	19.33

A-22 Certified Reference Material: The certified reference material GBW07312 (CRM), an aquatic sedimentary sample produced by the Chinese National Standard Material Bureau was digested; 0.5000 g of the (CRM) was weighed and digested using the microwave digestion method. The digestion reagent was (2.0 mL HF, 7.3 mL of HNO_3, 1.9 mL of HCl). The sample was fixed to 25.00 mL of 3.0M HCl after the dilution.

Spl ID	Spl weight (g)	Dil.Factor	Fixed Vol. (mL)	Pk Ht	Te/ µg/g
Spl1.#1	0.5000	40	50	36.61	0.41
Spl2.#2	0.5000	40	50	37.19	0.43
Spl2.#3	0.5000	40	50	37.51	0.44
Spl2.#4	0.5000	40	50	38.85	0.49

A-23 Total Te in tailing samples: Tailing number 2, 3,4 and 10 were digested using the microwave digestion method; 0.5000 g was weighed and digested using the microwave digestion method. The digestion reagent was (2.0 mL of HF, 7.3 mL of HNO3, 1.9mL of HCl). The final concentration was in 3.0M HCl.

Spl.ID	Dil.factor	Fix.vol mL	Pk Ht	Te µg/g
2ml HF.Tail#2.D100	100	25	59.58	56.26
2ml HF.Tail#4.D100	100	25	35.44	33.35
2ml HF.Tail#10.D100	100	25	70.62	66.74
Tail#ISP	100	25	16.17	15.06

A-24 Total Te in sediment samples: the same protocol used with the tailing above was used with the sediments.

Spl ID	Dil. Factor	Fix.vol mL	Te /µg/g	average	STD	SRD%
CrA14#1	200	25	3.32	3.21	0.72	22.47
CrA14#2	200	25	3.87			
CrA14#3	200	25	2.44			
CrA25# 1	200	25	12.08	10.90	1.10	10.09
CrA25# 2	200	25	9.91			
CrA25# 3	200	25	10.70			
CrF6# 1	200	25	11.71	10.70	1.05	9.77
CrF6# 2	200	25	10.77			
CrF6# 3	200	25	9.62			
CoA4# 1	200	25	3.88	3.46	0.48	13.83
CoA4# 2	200	25	3.55			
CoA4# 3	200	25	2.94			
CoB6# 1	200	25	3.96	3.57	0.47	13.13
CoB6# 2	200	25	3.05			
CoB6# 3	200	25	3.71			
Sed.CW1	100	25	26.57	25.28	1.98	7.81
Sed.CW2	100	25	23.00			
Sed.CW3	100	25	26.25			
Sed.MF1	100	25	19.11	20.80	1.69	8.13
Sed.MF2	100	25	20.80			
Sed.MF3	100	25	22.50			